Supporting Information

Indirect Synthesis of a Pair of Formal Methane Activation Products at a Phosphane / Borane Frustrated Lewis Pair

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† X-ray crystal structure analysis

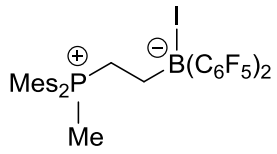
‡ Computational chemistry

General Information.

All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: melting points: TA-instruments DSC Q-20; elemental analyses: Foss–Heraeus CHNO-Rapid; IR: Varian 1300 FT-IR; NMR: Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{11}B, 160 MHz; ^{19}F, 470 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{11}B, 192 MHz; ^{19}F, 564 MHz). NMR chemical shifts are given relative to $SiMe_4$ and referenced to the respective solvent signal (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR, $\delta(H_3PO_4$, 85% in $D_2O) = 0$ for ^{31}P NMR]. NMR assignments were supported by additional 2D NMR experiments.

X-Ray diffraction: Data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **5** a badly disordered solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek, J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. CCDC deposition numbers are 1500836 to 1500838.

Synthesis of Compound 5



A mixture of dimesitylvinylphosphane (**7**) (80.0 mg, 0.27 mmol) and bis(pentafluorophenyl)borane (93.4 mg, 0.27 mmol, 1.0 eq.) was dissolved in dichloromethane (3 mL) and stirred for 20 min to give a yellow solution. Then methyl iodide [*Caution: MeI is toxic and must be handled with due care*] (22.0 μL, 0.35 mmol, 1.3 eq.) was added and after 50 min the solution started to become colorless. After stirring overnight the colorless reaction mixture was layered with *n*-pentane (9 mL) and stored at −30 °C for 2 h. The white precipitate was separated from the reaction solution *via* decantation, washed with *n*-pentane (4 mL) and dried *in vacuo*. Yield: 185 mg (0.24 mmol, 87%).

Melting point (DSC): 136 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3587 (w), 2925 (m, br), 2361 (w), 2340 (w), 1644 (s), 1606 (s), 1558 (s), 1522 (s), 1478 (s), 1382 (m), 1310 (m), 1276 (m), 1187 (m), 1120 (m), 1100 (m), 1029 (m), 977 (m), 933 (m), 899 (m), 872 (m), 854 (m), 824 (m), 782 (m), 741 (m), 710 (m), 655 (m), 635 (m), 596 (m), 553 (s), 542 (s), 477 (m), 465 (m), 445 (m), 429 (m), 409 (m).

Elemental analysis: Calc. for $C_{33}H_{29}BF_{10}IP$ (784.3 g/mol): C 50.54, H 3.73. Found: C 50.81, H 3.67.

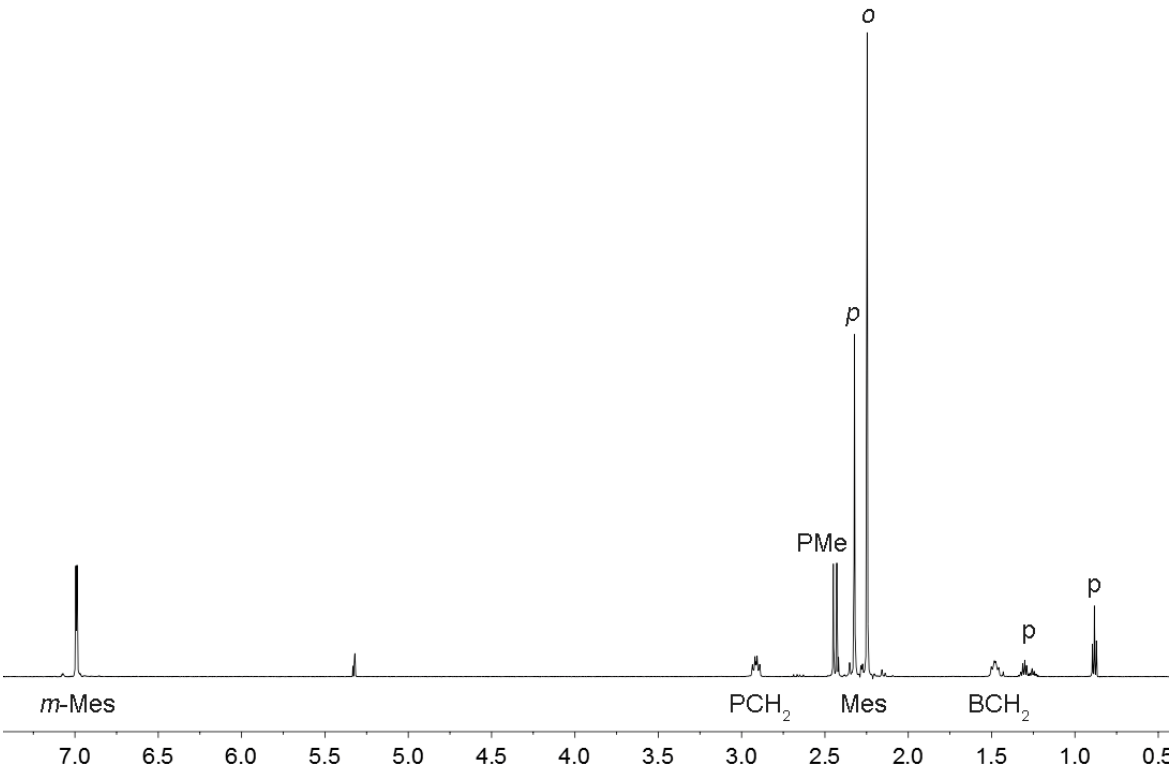
^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 6.99 (d, $^{4}J_{PH}$ = 4.2 Hz, 4H, *m*-Mes), 2.91 (m, 2H, PCH_2), 2.44 (d, $^{2}J_{PH}$ = 12.4 Hz, 3H, PCH_3), 2.32 (s, 6H, *p*-CH_3^{Mes}), 2.25 (s, 12H, *o*-CH_3^{Mes}), 1.48 (m, 2H, BCH_2).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 147.5 (dm, $^{1}J_{FC}$ ~ 241 Hz, C_6F_5), 144.9 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes), 141.8 (d, $^{2}J_{PC}$ = 9.7 Hz, *o*-Mes), 139.3 (dm, $^{1}J_{FC}$ ~ 248 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ ~ 247 Hz, C_6F_5), 132.9 (d, $^{3}J_{PC}$ = 11.4 Hz, *m*-Mes), 123.3 (br, *i*-C_6F_5), 118.6 (d, $^{1}J_{PC}$ = 79.2 Hz, *i*-Mes), 31.5 (d, $^{1}J_{PC}$ = 42.1 Hz, PCH_2), 23.5 (d, $^{3}J_{PC}$ = 4.6 Hz, *o*-CH_3^{Mes}), 21.3 (br, BCH_2), 21.1 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-CH_3^{Mes}), 16.3 (d, $^{1}J_{PC}$ = 53.2 Hz, PCH_3).

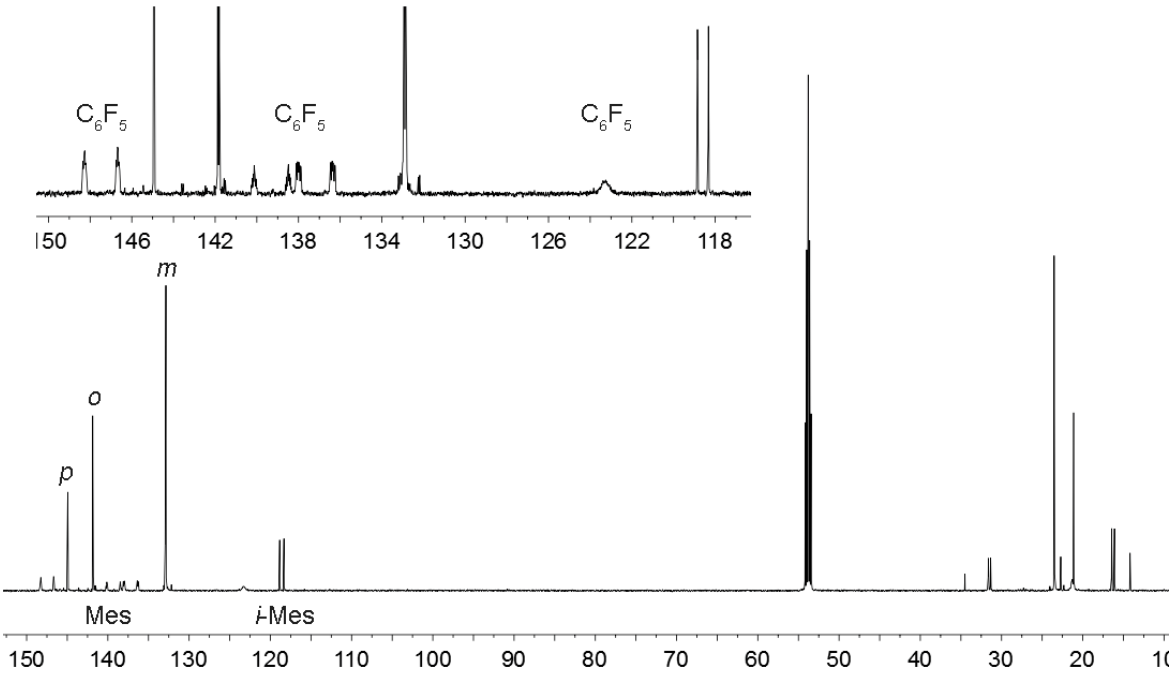
^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −130.9 (m, 2F, *o*-C_6F_5), −161.3 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −165.8 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 4.5].

$^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): $\delta = -7.4$ ($\nu_{1/2} \sim 450$ Hz).

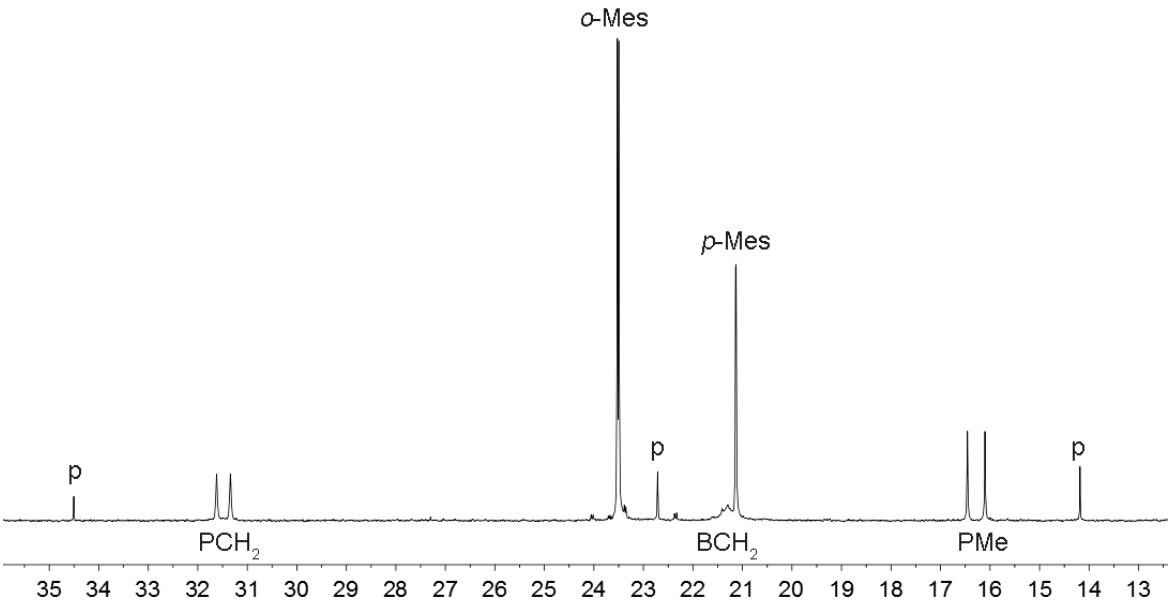
$^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): $\delta = 26.7$ ($\nu_{1/2} \sim 10$ Hz).



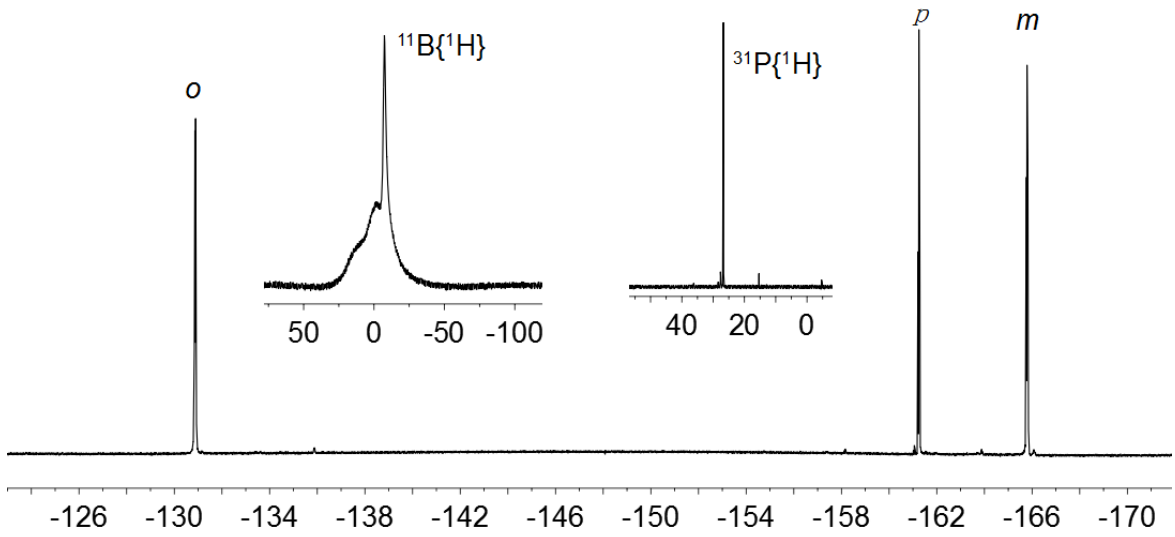
^1H NMR (600 MHz, $CD_2Cl_2^*$, 299 K) spectrum of compound **5** (p: *n*-pentane).



$^{13}C\{^1H\}$ NMR (151 MHz, $CD_2Cl_2^*$, 299 K) spectrum of compound **5**.



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2*, 299 K) spectrum of compound **5** (p: *n*-pentane).

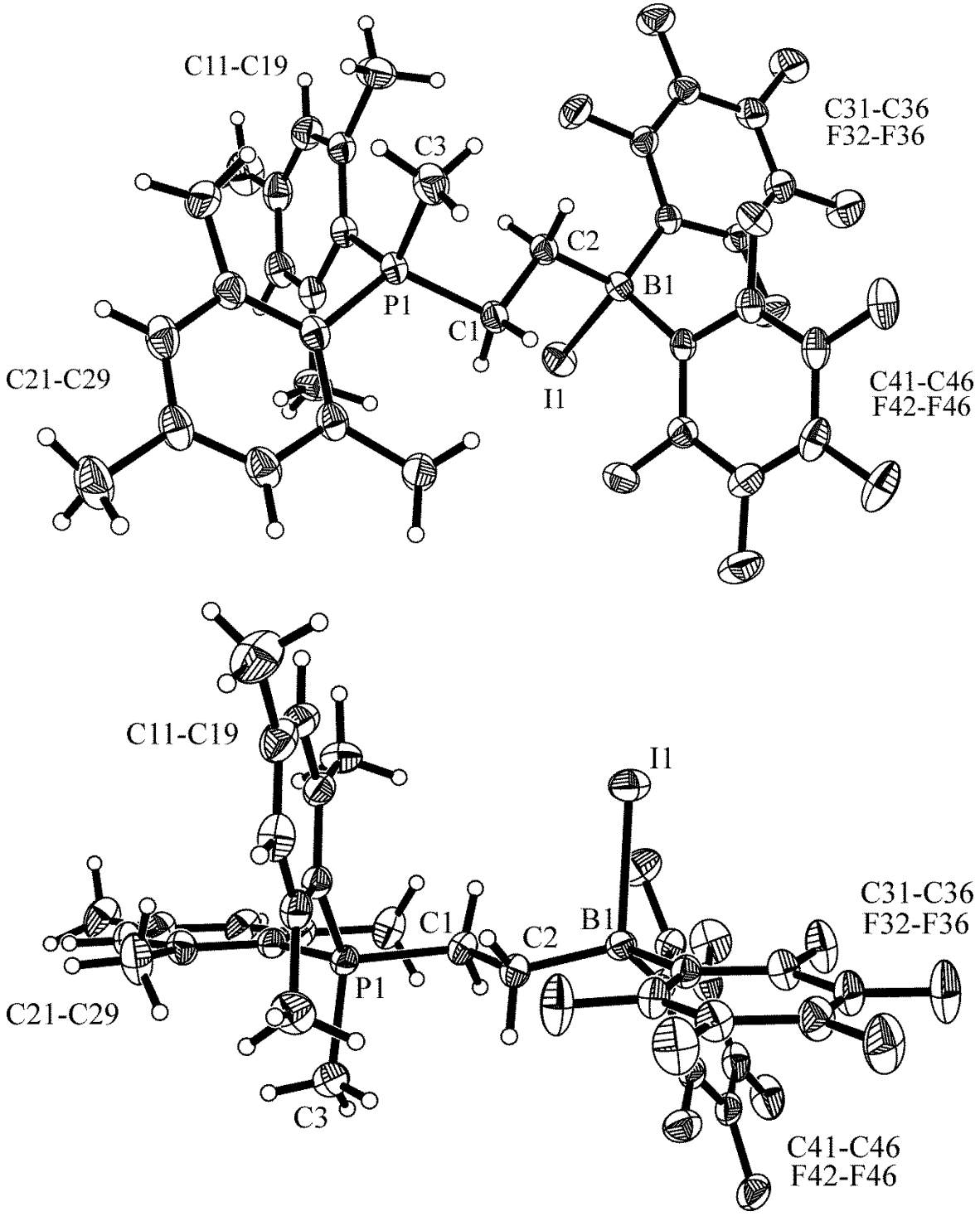


^{19}F NMR (564 MHz, CD_2Cl_2, 299 K), $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 299 K) and $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectra of compound **5**.

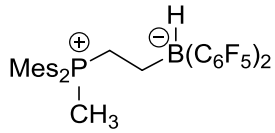
Crystals suitable for the X-ray single crystal structure analysis were grown by slow concentration of a dichloromethane solution of compound **5** at –30 °C.

X-ray crystal structure analysis of compound 5: formula $C_{33}H_{29}BF_{10}IP$, M = 784.24, colourless crystal, 0.37 x 0.15 x 0.07 mm, a = 10.7065(2), b = 11.5683(8), c = 16.2976(5) Å, α = 87.146(3), β = 83.941(2), γ = 64.082(4)°, V = 1805.4(1) Å^3, ρ_{calc} = 1.443 gcm^{-3}, μ = 8.041 mm^{-1}, empirical absorption correction (0.154 ≤ T ≤ 0.602), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 20891 reflections collected (±h, ±k, ±l), 6100 independent (R_{int} =

0.039) and 5917 observed reflections [$I>2\sigma(I)$], 422 refined parameters, R = 0.034, wR^2 = 0.094, max. (min.) residual electron density 0.35 (-0.67) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of Compound 6



Chlorodimethylsilane (28.0 µL, 0.252 mmol, 2.4 eq.) was added to a colorless solution of compound **5** (82.3 mg, 0.105 mmol) in dichloromethane (3 mL). After stirring for 30 min the colorless reaction solution was layered with *n*-pentane (8 mL) and stored at −30 °C for 6 d. The precipitated white crystals were separated from the reaction solution *via* decantation, washed with *n*-pentane (4 mL) and dried *in vacuo*. Yield: 61 mg (0.093 mmol, 88%).

Melting point (DSC): 191 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 4350 (w), 3747 (w), 3445 (w), 2992 (m), 2917 (m), 2850 (w), 2336 (s), 2184 (w), 2114 (w), 1640 (m), 1605 (s), 1555 (m), 1508 (s), 1461 (s), 1412 (m), 1380 (m), 1309 (w), 1268 (s), 1185 (s), 1132 (m), 1099 (s), 1079 (s), 1030 (m), 972 (s), 918 (m), 901 (s), 861 (m), 778 (m), 748 (m), 710 (w), 633 (m), 595 (w), 553 (m), 458 (w), 415 (m).

Elemental analysis: Calc. for $C_{33}H_{30}BF_{10}P$ (658.4 g/mol): C 60.20, H 4.59. Found: C 60.03, H 4.39.

^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 6.96 (d, $^{4}J_{PH}$ = 4.1 Hz, 4H, *m*-Mes), 2.75 (br m, BH), 2.72 (m, 2H, PCH_2), 2.39 (d, $^{2}J_{PH}$ = 12.5 Hz, 3H, PCH_3), 2.31 (s, 6H, *p*-CH_3^{Mes}), 2.24 (s, 12H, *o*-CH_3^{Mes}), 0.97 (br, 2H, BCH_2).

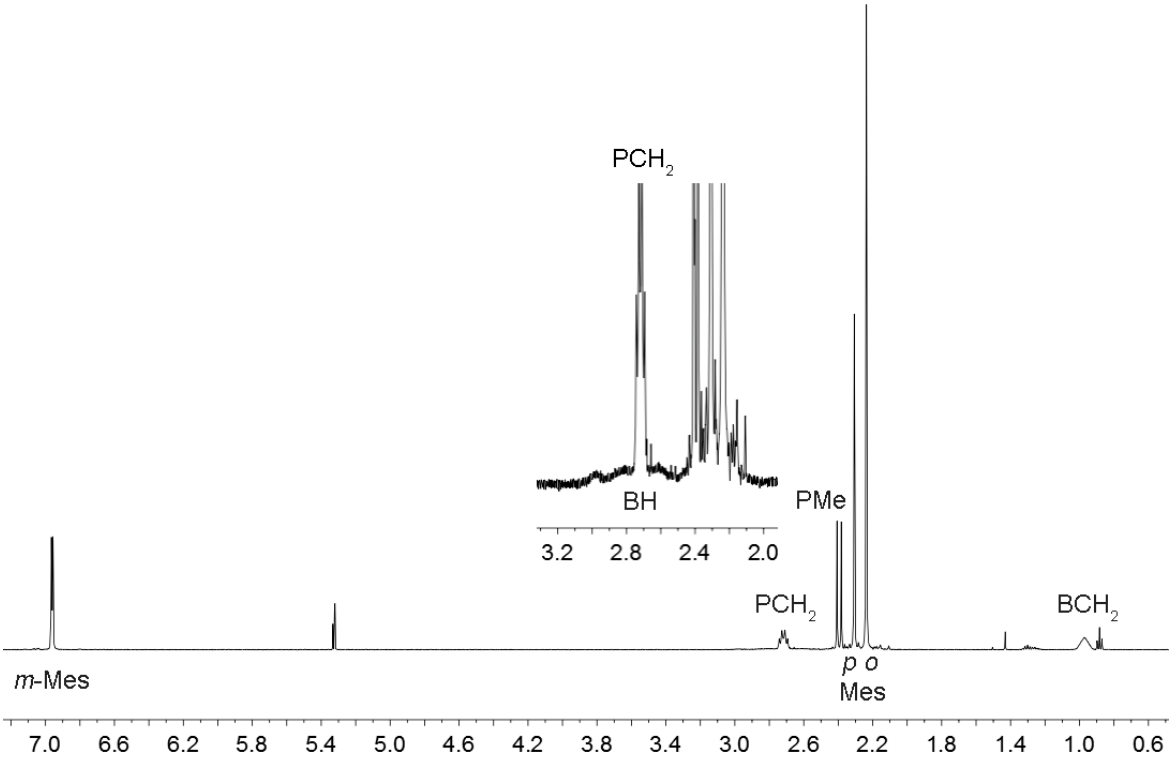
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 148.4 (dm, $^{1}J_{FC}$ ~ 235 Hz, C_6F_5), 144.5 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Mes), 141.9 (d, $^{2}J_{PC}$ = 9.4 Hz, *o*-Mes), 138.0 (dm, $^{1}J_{FC}$ ~ 243 Hz, C_6F_5), 136.8 (dm, $^{1}J_{FC}$ ~ 247 Hz, C_6F_5), 132.7 (d, $^{3}J_{PC}$ = 11.2 Hz, *m*-Mes), 126.8 (br, *i*-C_6F_5), 119.5 (d, $^{1}J_{PC}$ = 77.8 Hz, *i*-Mes), 32.7 (d, $^{1}J_{PC}$ = 36.3 Hz, PCH_2), 23.5 (d, $^{3}J_{PC}$ = 4.6 Hz, *o*-CH_3^{Mes}), 21.1 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-CH_3^{Mes}), 16.0 (d, $^{1}J_{PC}$ = 54.3 Hz, PCH_3), 14.6 (br m, BCH_2).

^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.9 (m, 2F, *o*-C_6F_5), −164.4 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −166.9 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 2.5].

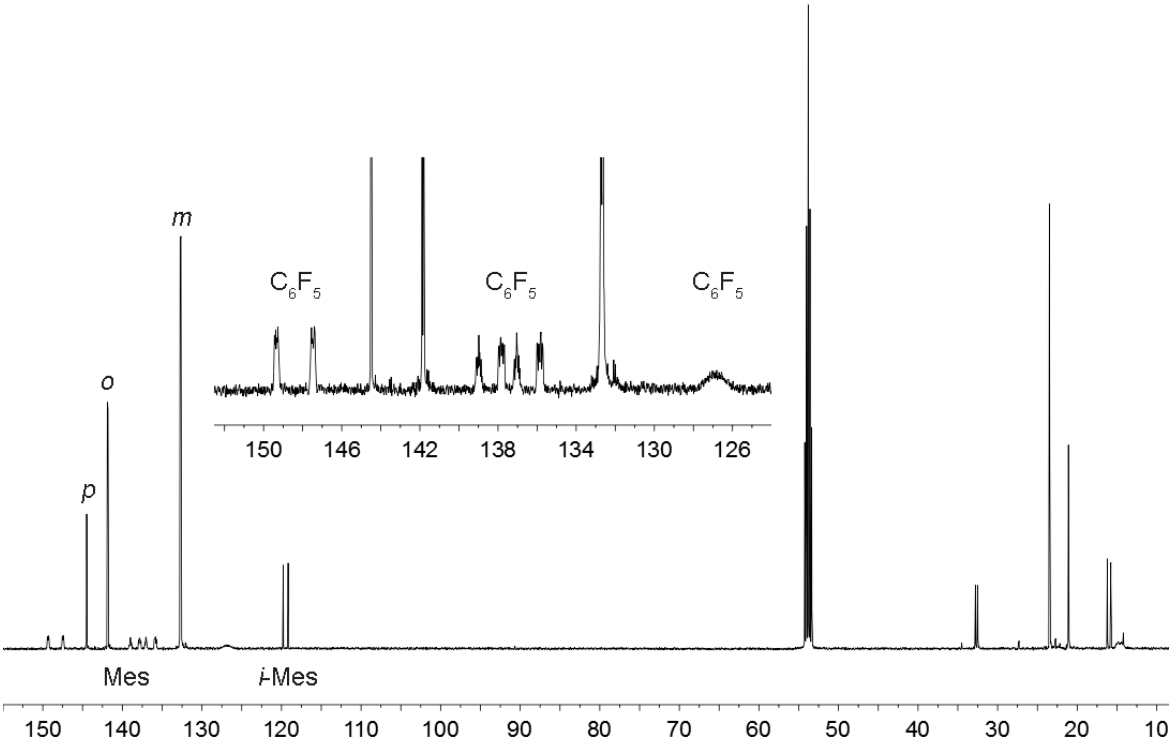
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = –19.7 ($\nu_{1/2}$ ~ 60 Hz).

^{11}B NMR (160 MHz, CD_2Cl_2, 299 K): δ = –19.7 (d, $^{1}J_{BH}$ ~ 90 Hz).

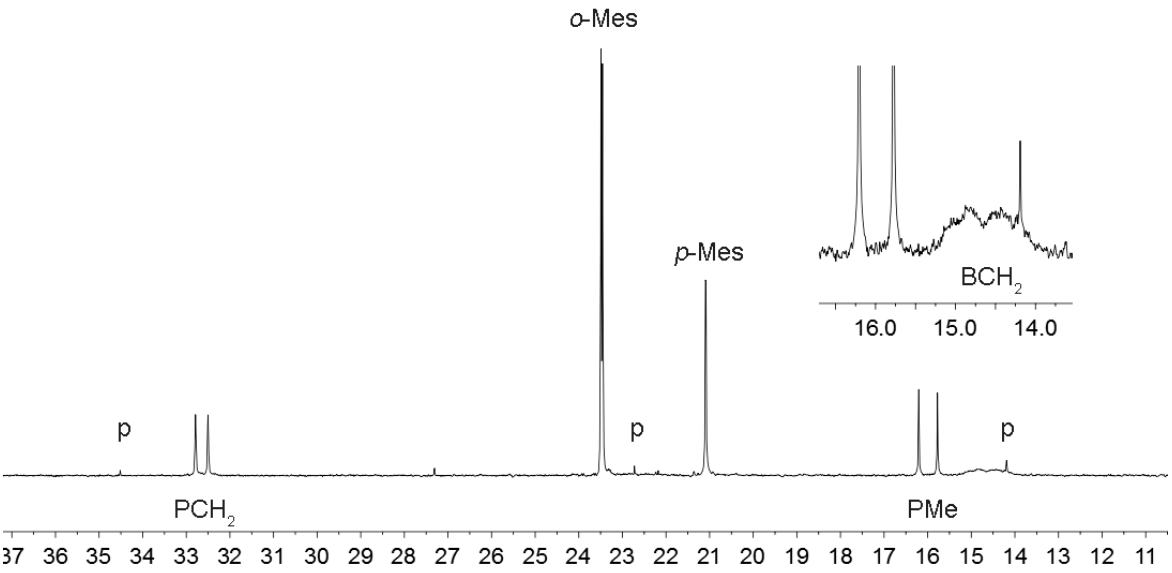
^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 25.8 (d, *J* = 25.0 Hz).



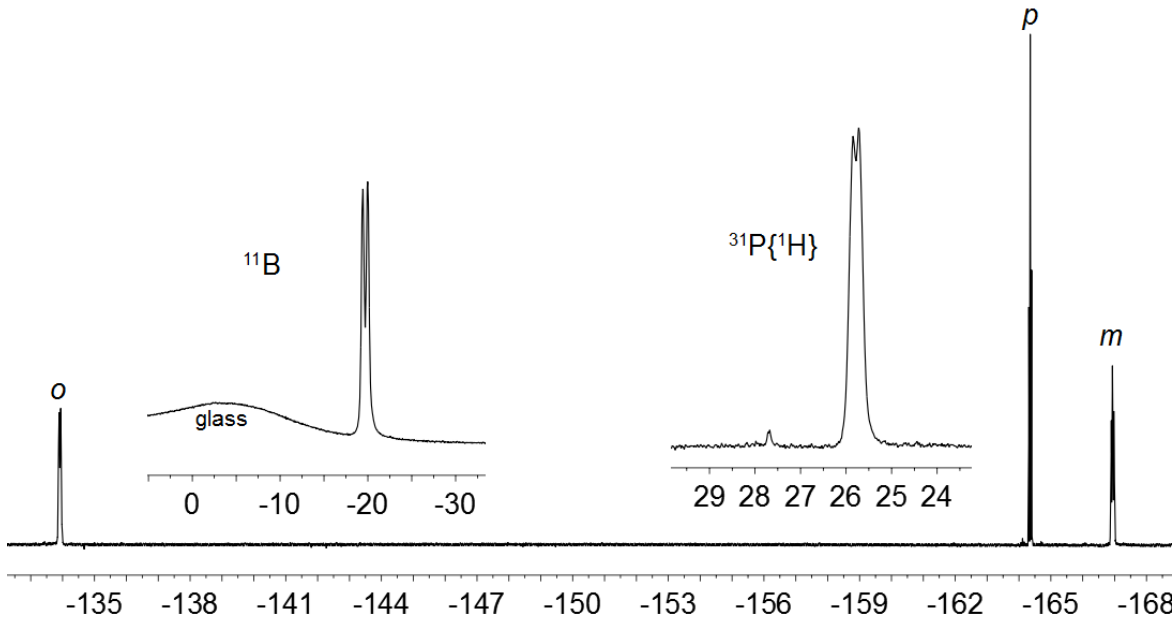
^{1}H NMR (500 MHz, CD_2Cl_2*, 299 K) spectrum of compound **6** (p: *n*-pentane).



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2*, 299 K) spectrum of compound **6**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2*, 299 K) spectrum of compound **6** (p: *n*-pentane).

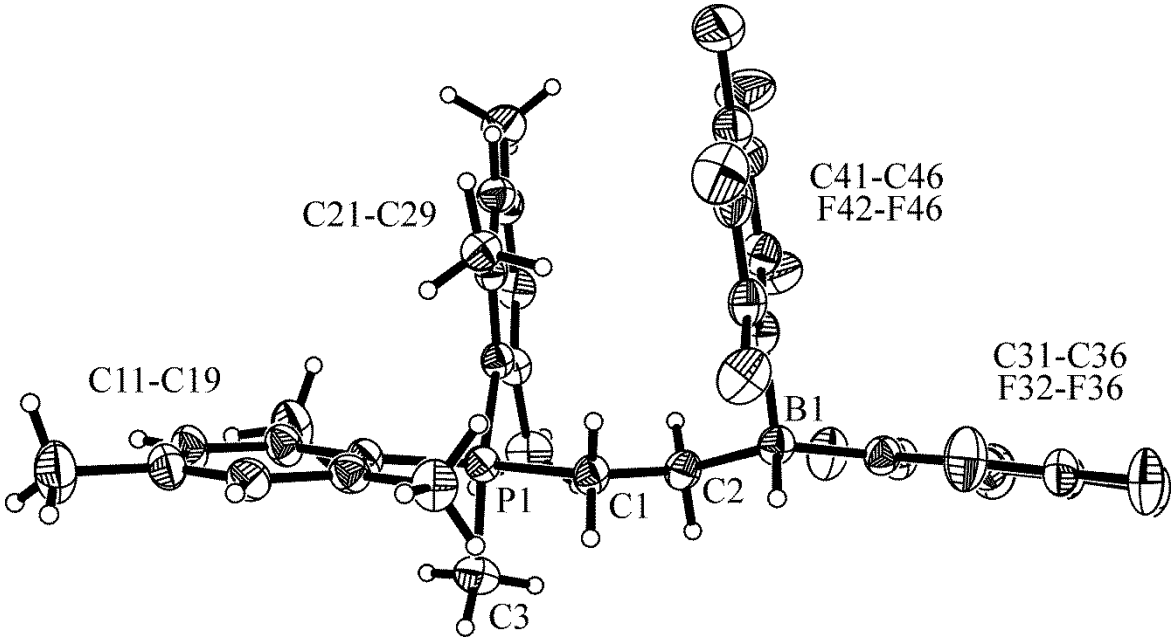


^{19}F NMR (470 MHz, CD_2Cl_2, 299 K), $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 299 K) and ^{11}B NMR (160 MHz, CD_2Cl_2, 299 K) spectra of compound **6**.

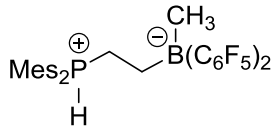
Crystals suitable for the X-ray single crystal structure analysis were grown from a deuterated dichloromethane solution of compound **6** which was layered with *n*-pentane and stored at −30 °C.

X-ray crystal structure analysis of compound 6: formula $C_{33}H_{30}BF_{10}P$, M = 658.35, colourless crystal, 0.20 x 0.12 x 0.08 mm, a = 13.8025(2), b = 13.6770(2), c = 16.4268(3) Å, β = 98.949(1) °, V = 3063.3(1) $Å^3$, ρ_{calc} = 1.428 gcm^{-3}, μ = 0.174 mm^{-1}, empirical absorption correction (0.966 ≤ T ≤ 0.986), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ

scans, 21108 reflections collected (±*h*, ±*k*, ±*l*), 5311 independent (R_{int} = 0.050) and 4203 observed reflections [$I>2\sigma(I)$], 417 refined parameters, R = 0.058, wR^2 = 0.141, max. (min.) residual electron density 0.22 (-0.20) e.Å^{-3}, the hydrogen position at B1 atom was refined freely; others hydrogen atoms were calculated and refined as riding atoms.



Synthesis of Compound 9



A mixture of dimesitylvinylphosphane (**7**) (80.0 mg, 0.27 mmol) and bis(pentafluorophenyl)-borane (93.4 mg, 0.27 mmol, 1.0 eq.) was dissolved in toluene (3 mL) and stirred for 15 min to give a yellow solution. Upon addition of Cp_2ZrMe_2 (67.9 mg, 0.27 mmol, 1.0 eq.) the solution turned orange immediately. Subsequent addition of degassed distilled water (7.5 µL, 0.42 mmol, 1.5 eq.) led to a colorless solution with a white precipitation within 15 min. After stirring for 1.5 h the reaction mixture was filtered through celite to remove the white solid. The reaction solution was concentrated, layered with *n*-pentane (4 mL) and stored at –30 °C overnight. A white solid had precipitated and was separated from the solution *via* decantation, washed with *n*-pentane (2 mL) and dried *in vacuo*. Yield: 168 mg (0.26 mmol, 95%).

Melting point (DSC): 165 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3751 (w), 3030 (w), 2928 (m), 2828 (w), 1639 (m), 1604 (s), 1558 (m), 1541 (m), 1510 (s), 1451 (s), 1380 (m), 1294 (m), 1267 (s), 1174 (s), 1121 (s), 1079 (s), 1030 (m), 1000 (m), 949 (s), 908 (m), 858 (m), 827 (m), 782 (m), 766 (m), 732 (s), 703 (m), 641 (m), 604 (m), 570 (w), 556 (m), 511 (w), 464 (w), 436 (w), 413 (w).

Elemental analysis: Calc. for $C_{33}H_{30}BF_{10}P$ (658.4 g/mol): C 60.20, H 4.59. Found: C 59.62, H 4.43.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.36 (dt, $^{1}J_{PH}$ = 469.2 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, PH), 7.05 (d, $^{4}J_{PH}$ = 4.4 Hz, 4H, *m*-Mes), 2.61 (m, 2H, PCH_2), 2.38 (s, 12H, *o*-CH_3^{Mes}), 2.34 (s, 6H, *p*-CH_3^{Mes}), 1.21 (m, 2H, BCH_2), 0.13 (br s, 3H, BCH_3).

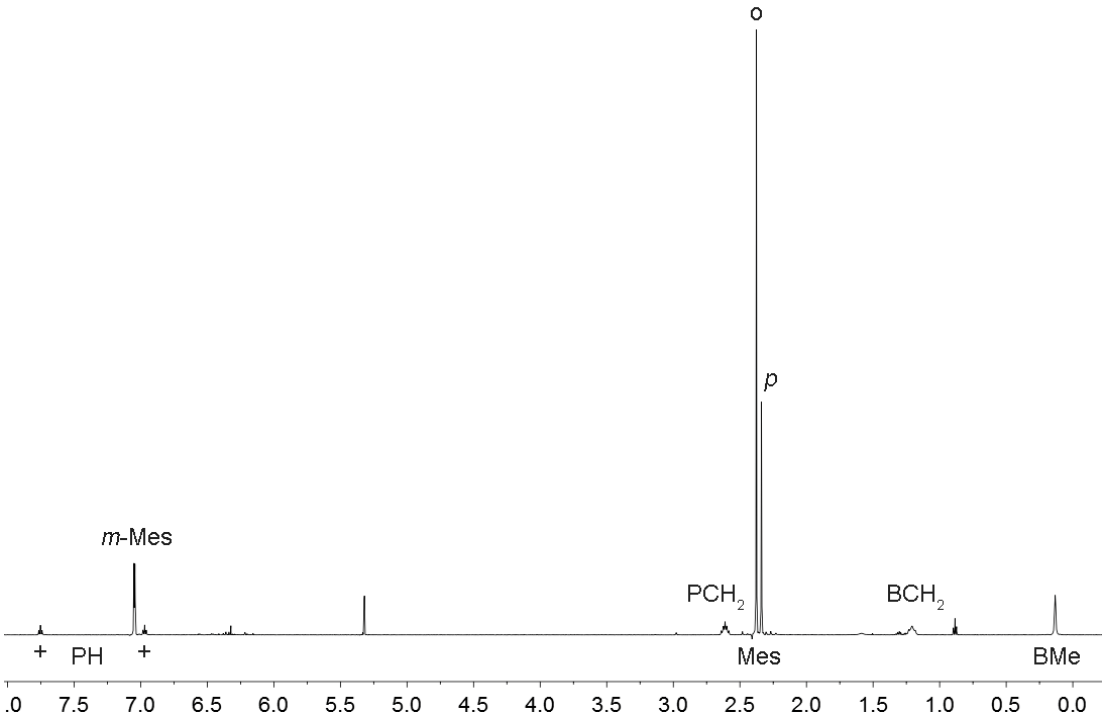
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 148.4 (dm, $^{1}J_{FC}$ ~ 234 Hz, C_6F_5), 145.9 (d, $^{4}J_{PC}$ = 2.5 Hz, *p*-Mes), 143.3 (d, $^{2}J_{PC}$ = 9.6 Hz, *o*-Mes), 137.7 (dm, $^{1}J_{FC}$ ~ 243 Hz, C_6F_5), 136.9 (dm, $^{1}J_{FC}$ ~ 247 Hz, C_6F_5), 132.1 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*-Mes), 130.2 (br, *i*-C_6F_5), 113.4 (d, $^{1}J_{PC}$ = 75.7 Hz, *i*-Mes), 25.0 (d, $^{1}J_{PC}$ = 34.1 Hz, PCH_2), 23.0 (br m, BCH_2), 22.2 (d, $^{3}J_{PC}$ = 6.7 Hz, *o*-CH_3^{Mes}), 21.4 (d, $^{5}J_{PC}$ = 1.3 Hz, *p*-CH_3^{Mes}), 9.4 (br m, BCH_3).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −134.0 (m, 2F, *o*-C_6F_5), −164.7 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −166.9 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 2.2].

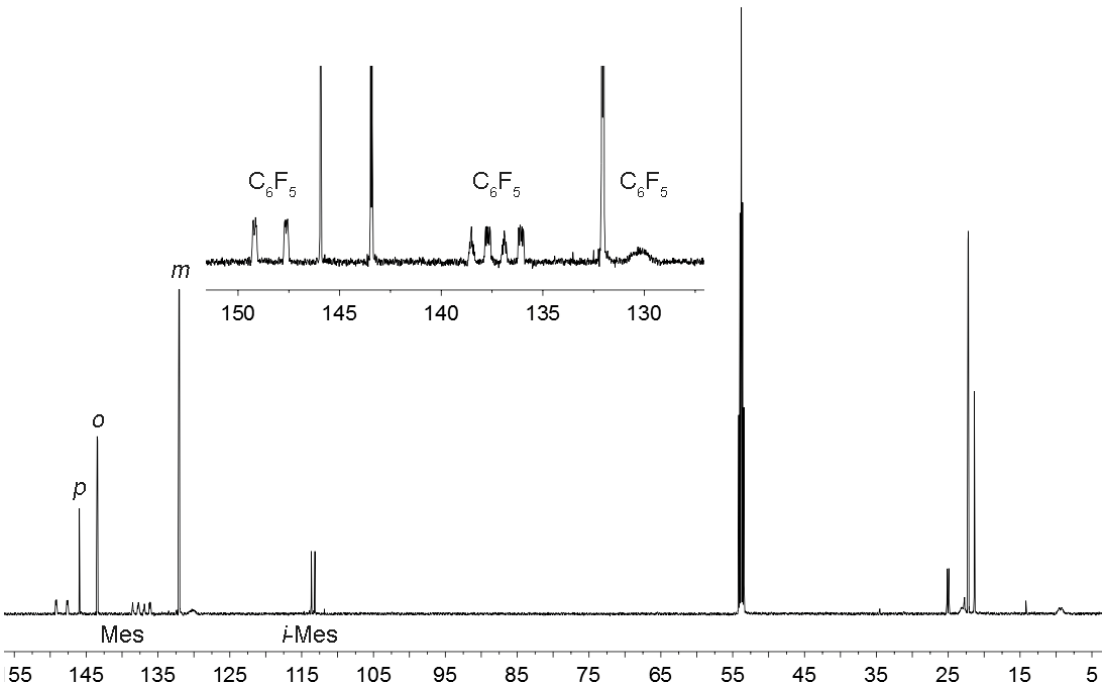
^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = –12.7 ($\nu_{1/2}$ ~ 60 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = –2.1 (d, *J* ~ 15 Hz).

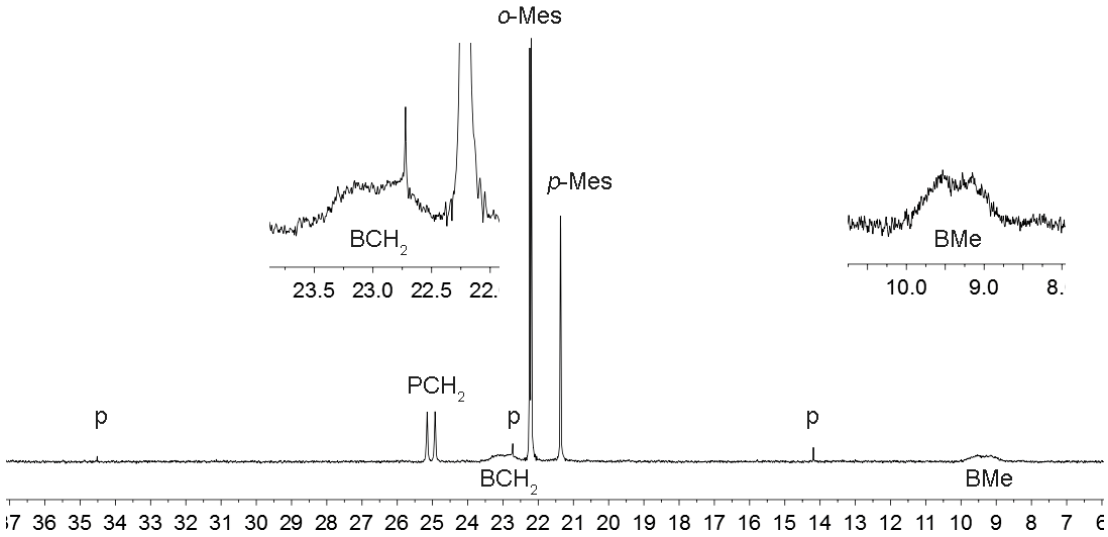
^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = –2.1 (d, $^1J_{PH}$ ~ 470 Hz).



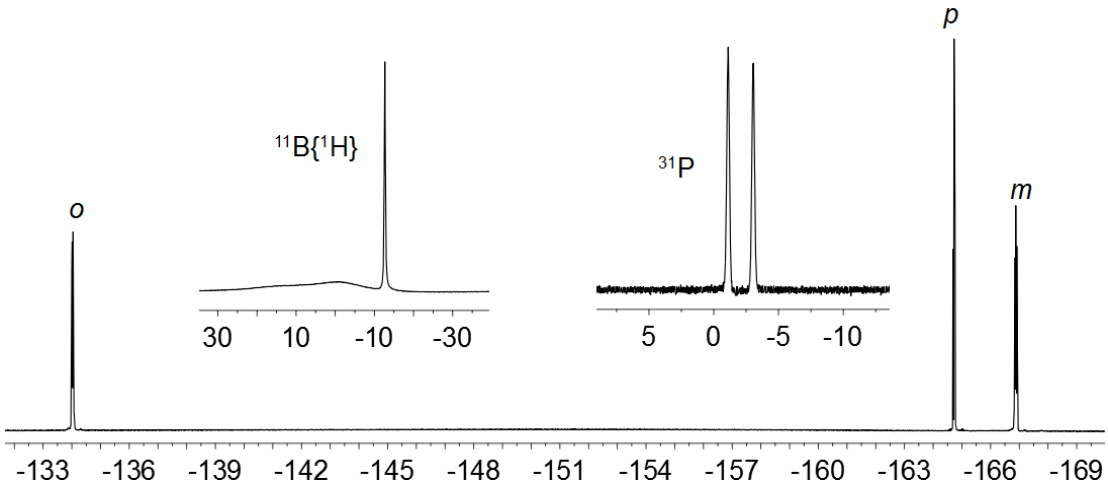
^{1}H NMR (600 MHz, CD_2Cl_2*, 299 K) spectrum of compound **9**.



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2*, 299 K) spectrum of compound **9**.



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2*, 299 K) spectrum of compound **9** (p: *n*-pentane).

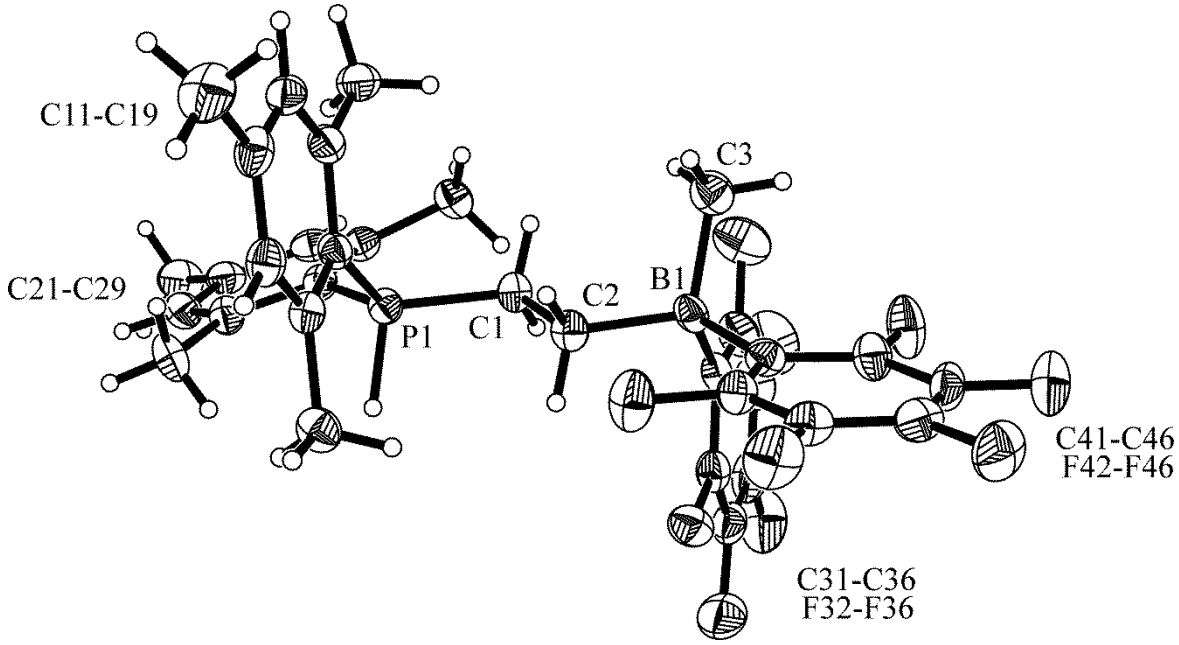


^{19}F NMR (564 MHz, CD_2Cl_2, 299 K), ^{31}P NMR (243 MHz, CD_2Cl_2, 299 K) and $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectra of compound **9**.

Crystals suitable for the X-ray single crystal structure analysis were obtained from a solution of compound **9** in dichloromethane which was layered with *n*-pentane and stored at −30 °C.

X-ray crystal structure analysis of compound 9: formula $C_{33}H_{30}BF_{10}P$, M = 658.35, colourless crystal, 0.10 x 0.07 x 0.01 mm, a = 11.7033(2), b = 14.0272(3), c = 18.5652(6) Å, β = 92.943(1) °, V = 3043.7(1) Å^3, ρ_{calc} = 1.437 gcm^{-3}, μ = 0.175 mm^{-1}, empirical absorption correction (0.982 ≤ T ≤ 0.998), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 25020 reflections collected ($\pm h$, $\pm k$, $\pm l$), 6095 independent (R_{int} = 0.122) and 3318 observed reflections [$I>2\sigma(I)$], 417 refined parameters, R = 0.095, wR^2 = 0.169, max. (min.) residual

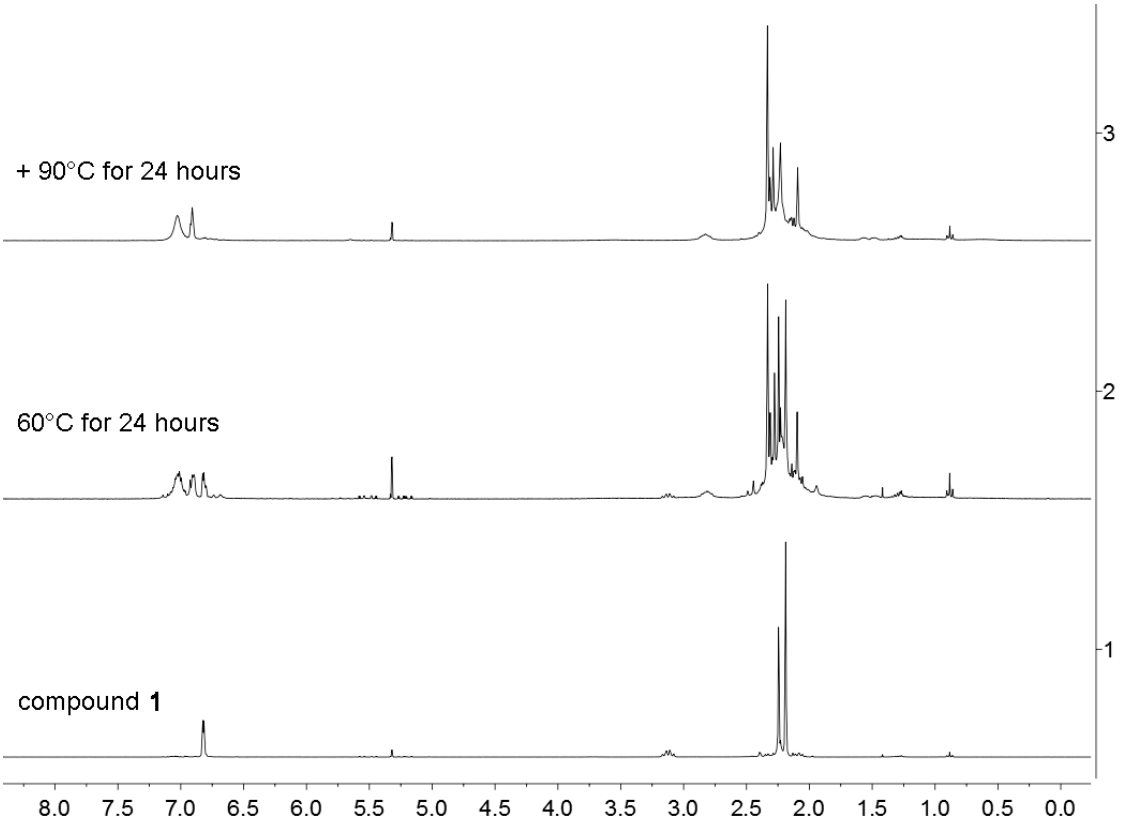
electron density 0.28 (-0.29) e.Å^{-3}, the hydrogen position at P1 atom was refined freely; others hydrogen atoms were calculated and refined as riding atoms.



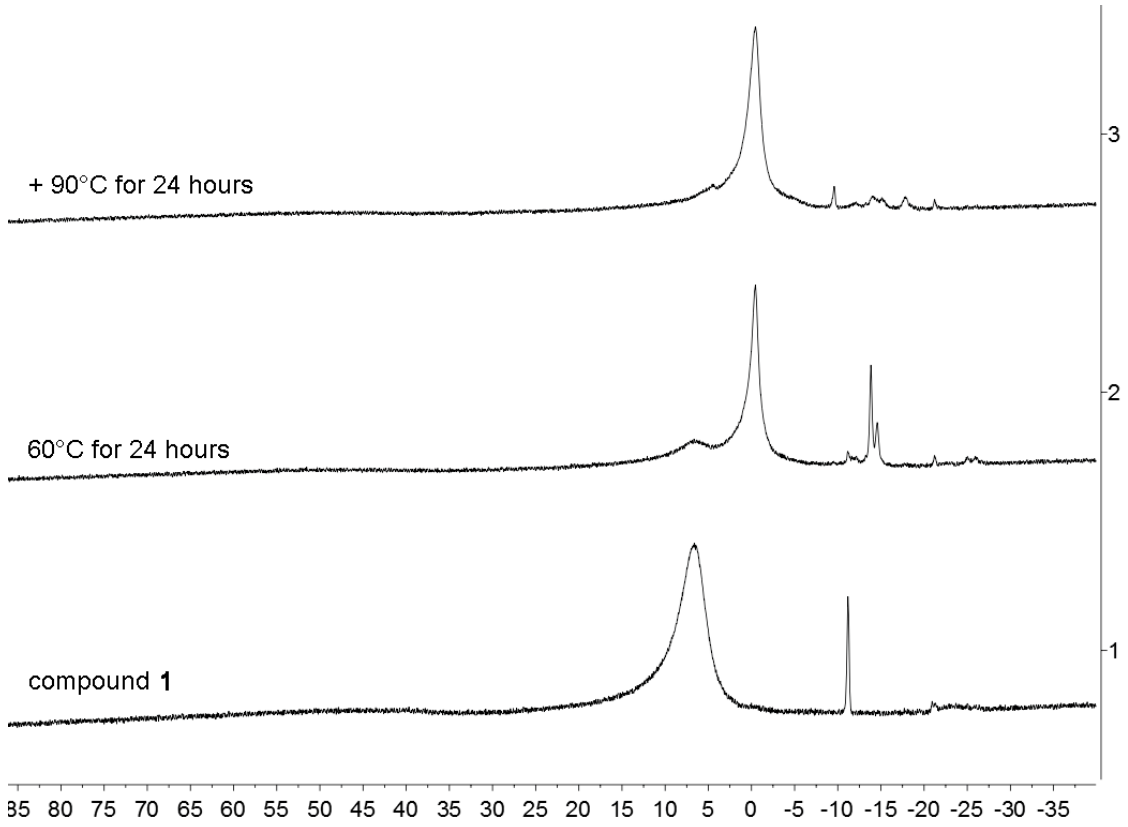
Heating of compounds 1, 6 and 9 (NMR scale)

A solution of (a) compound **1** [in situ generated by using compound **7** (80.0 mg, 0.27 mmol) and $HBC_6F_5)_2$ (93.4 mg, 0.27 mmol) in CD_2Cl_2 (1 mL)], (b) compound **6** (50 mg, 0.076 mmol), and compound **9** (50 mg, 0.076 mmol), respectively, in CD_2Cl_2 was heated stepwise from 60 °C (24h) to 90 °C (24h).

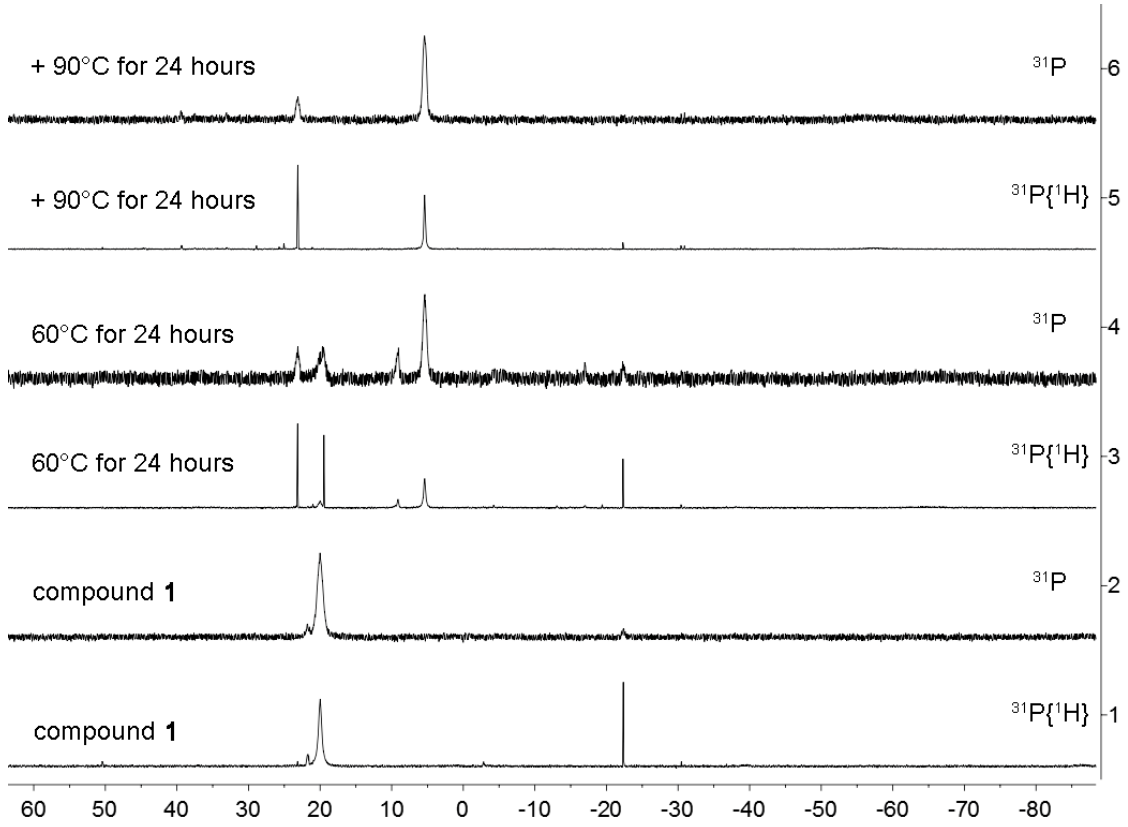
Compound **1**:



^{1}H NMR (300 MHz, CD_2Cl_2) spectra of (1) in situ generated compound **1** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.

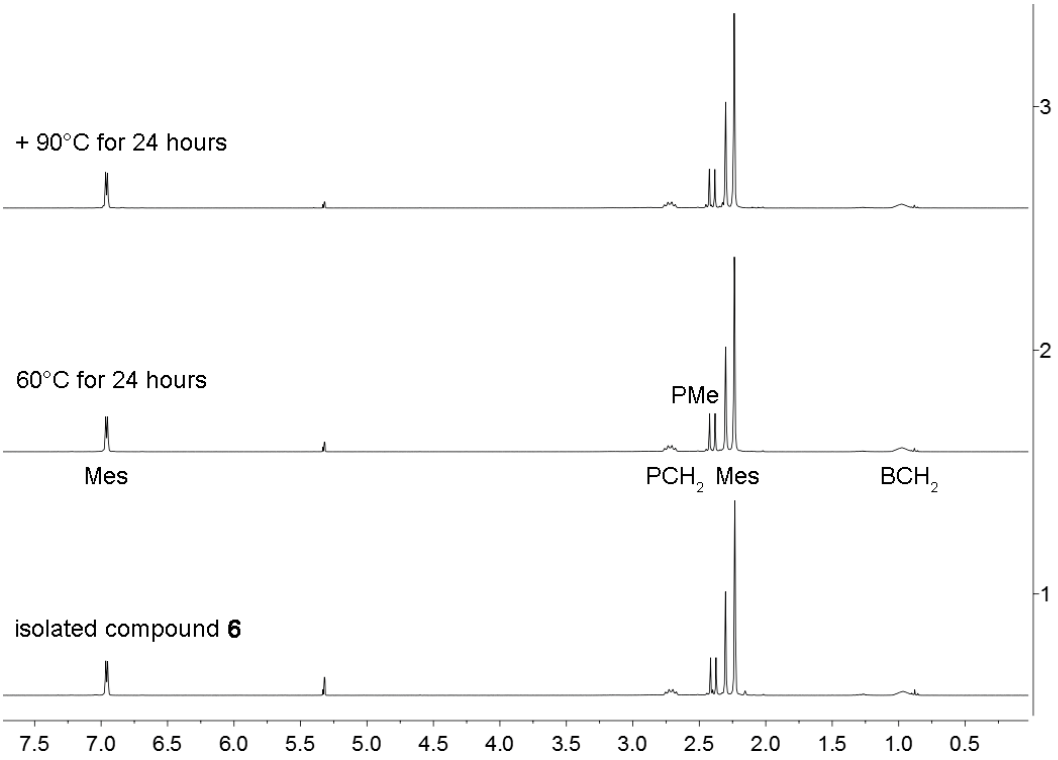


^{11}B NMR (96 MHz, CD_2Cl_2) spectra of (1) in situ generated compound **1** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.

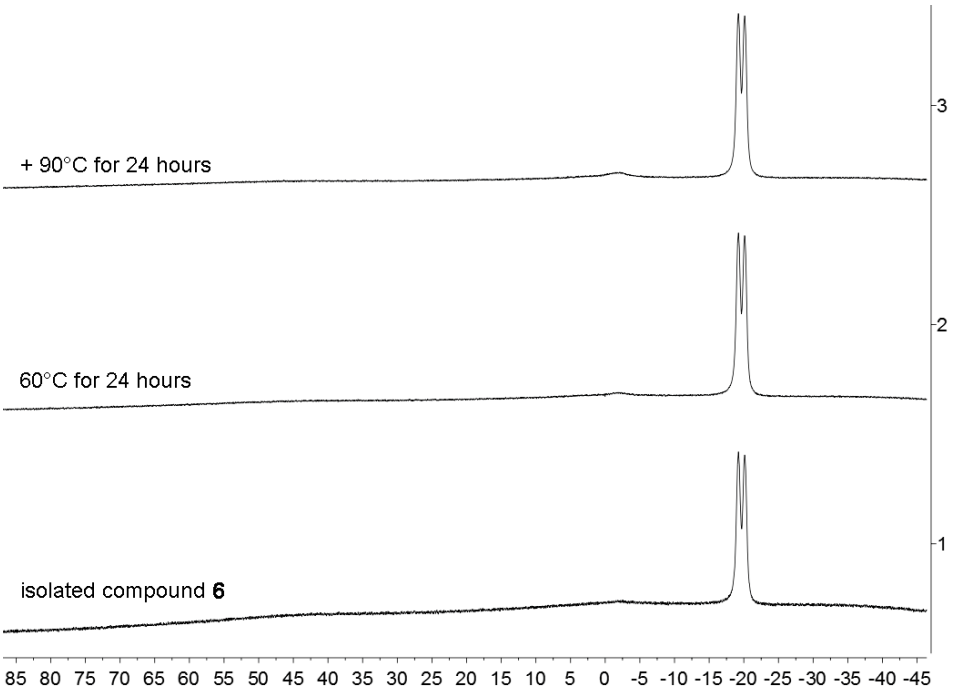


(1,3,5) $^{31}P\{^1H\}$ and (2,4,6) ^{31}P NMR (121 MHz, CD_2Cl_2) spectra of (1,2) in situ generated compound **1** and after heating first (3,4) at 60°C for 24 hours and then (5,6) at 90°C for 24 hours.

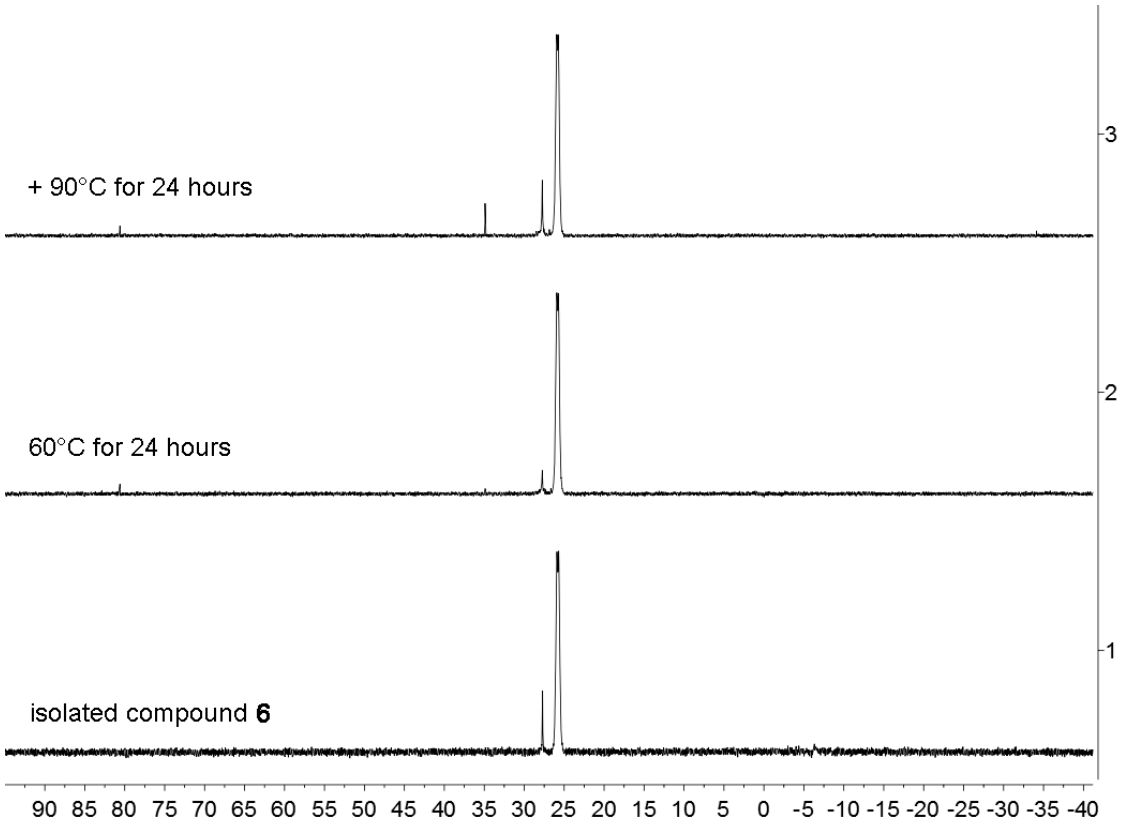
Compound **6**:



^{1}H NMR (300 MHz, CD_2Cl_2) spectra of (1) isolated compound **6** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.

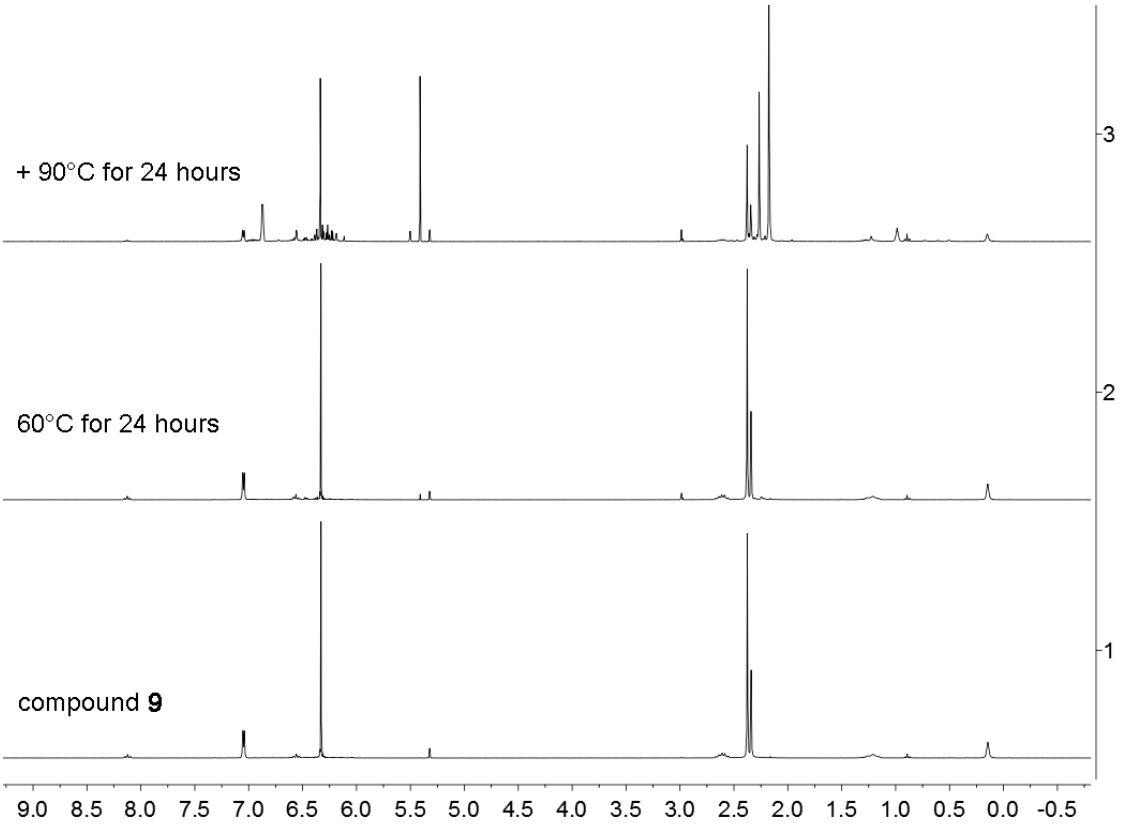


^{11}B NMR (96 MHz, CD_2Cl_2) spectra of (1) isolated compound **6** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.

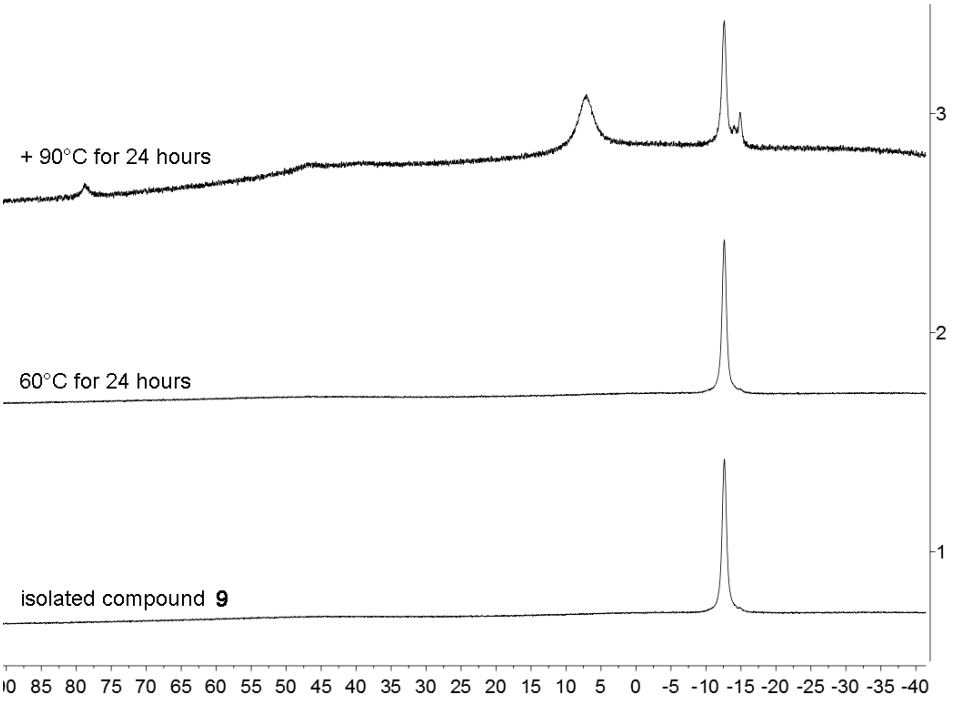


$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) spectra of (1) isolated compound **6** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.

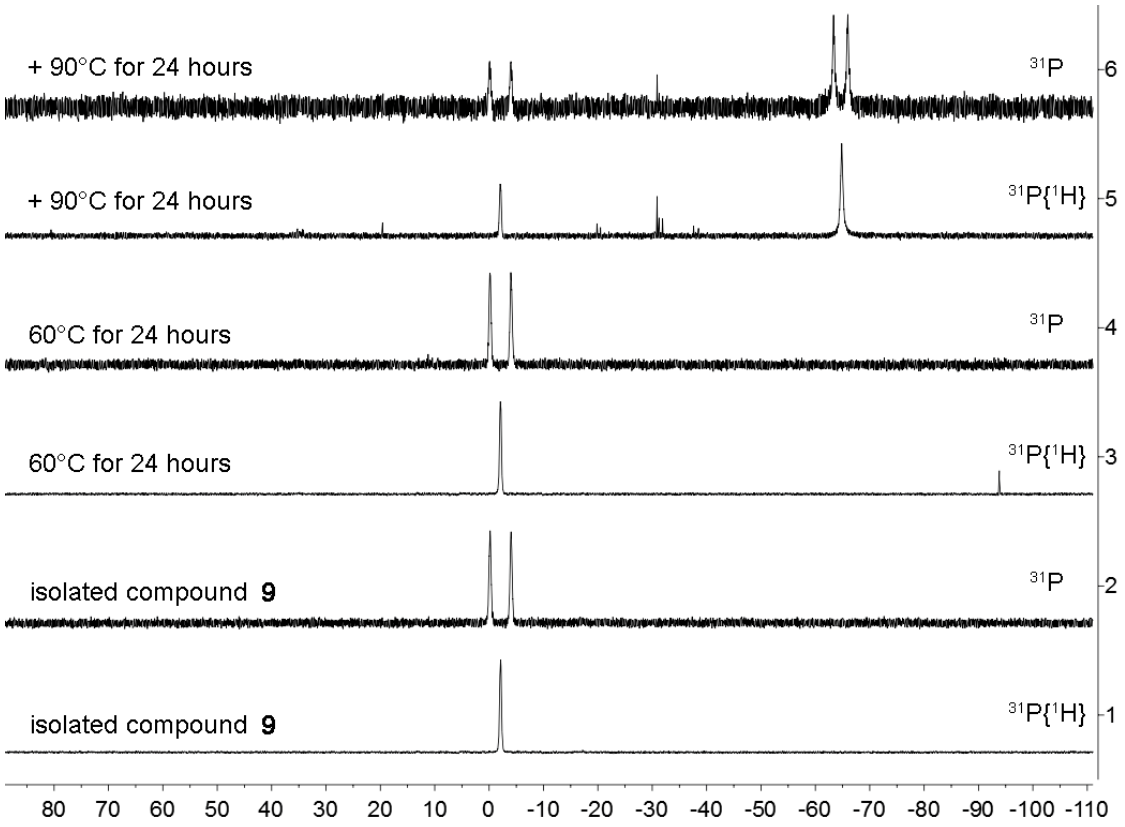
Compound **9**:



^{1}H NMR (300 MHz, CD_2Cl_2) spectra of (1) isolated compound **9** [admixed with some Cp_2Zr-contamination] and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.



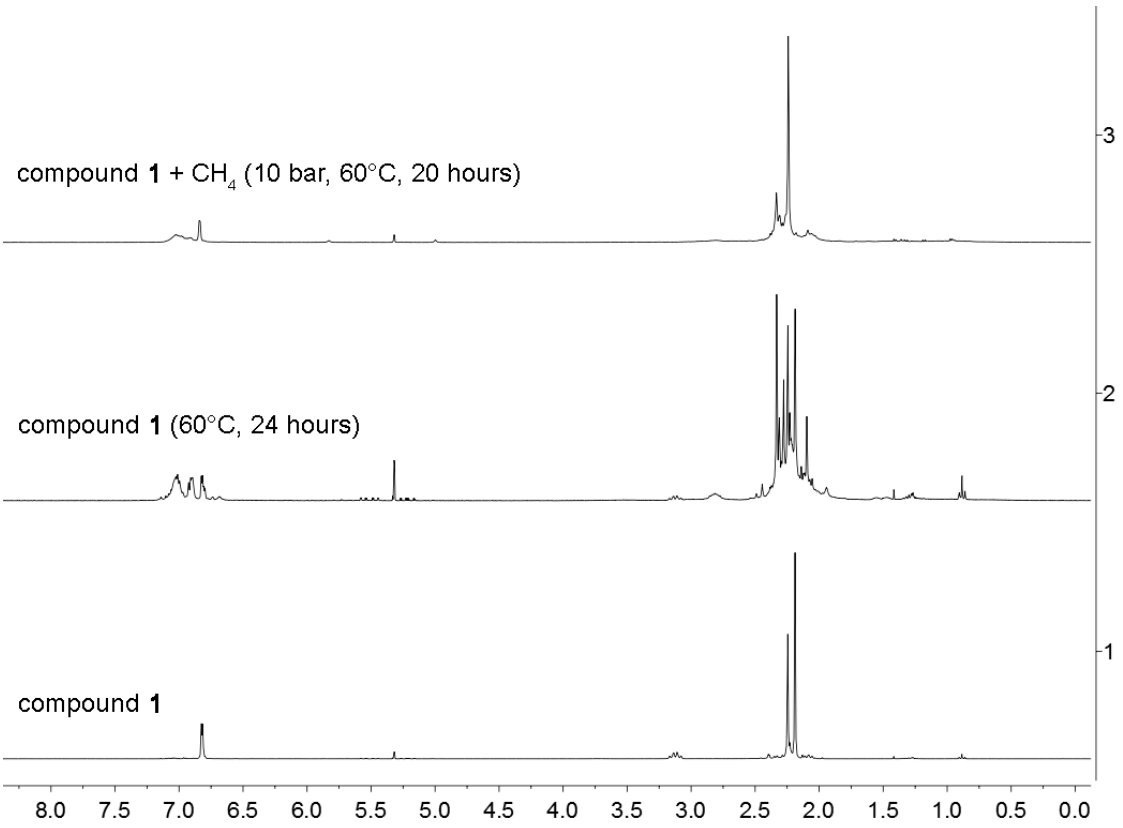
^{11}B NMR (96 MHz, CD_2Cl_2) spectra of (1) isolated compound **9** and after heating first (2) at 60°C for 24 hours and then (3) at 90°C for 24 hours.



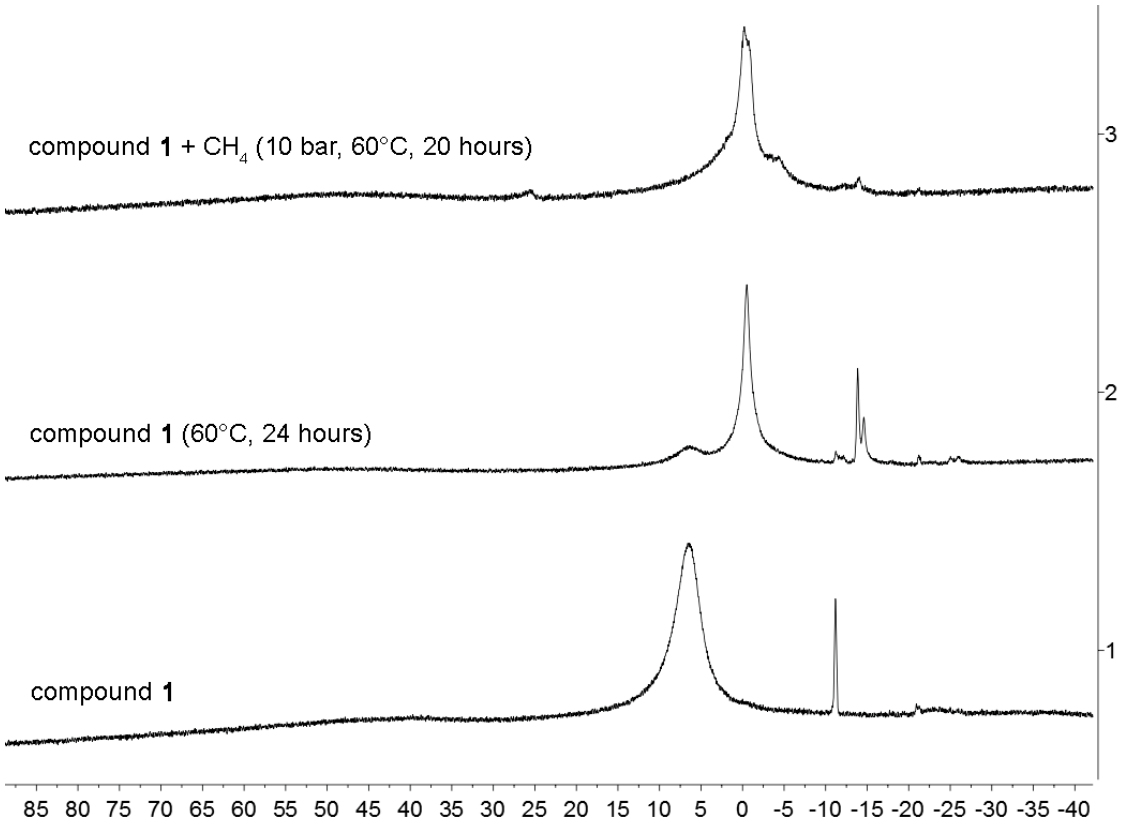
(1,3,5) $^{31}P\{^{1}H\}$ and (2,4,6) ^{31}P NMR (121 MHz, CD_2Cl_2) spectra of (1,2) isolated compound **9** and after heating first (3,4) at 60°C for 24 hours and then (5,6) at 90°C for 24 hours.

Reaction of compounds 1 with CH_4

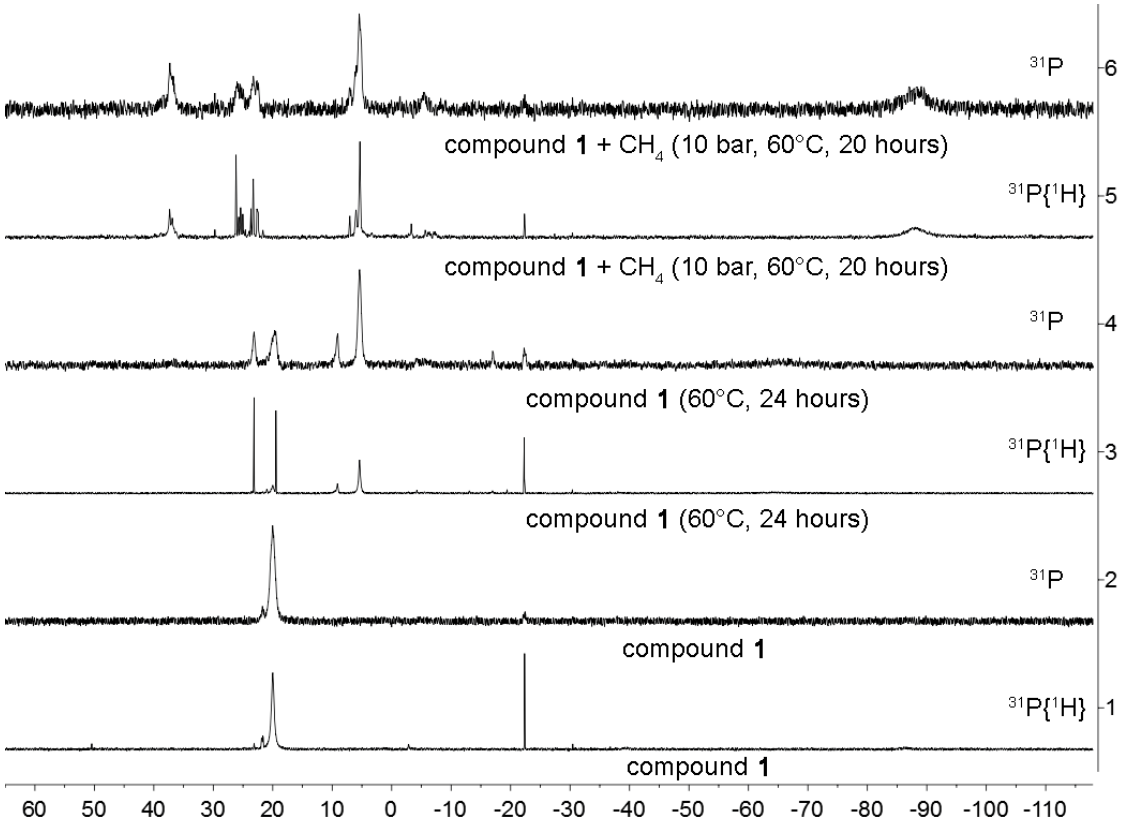
A solution of in situ generated compound **1** [compound 7 (40mg, 0.14 mmol) and $HBC_6F_5)_2$ (46.7 mg, 0.14 mmol) in CD_2Cl_2 (1 mL)] was exposed to methane (10 bar) for 20 h at 60 °C.



^{1}H NMR (300 MHz, CD_2Cl_2) spectra of the reaction of in situ generated compound **1** with methane (10 bar) at 60°C for 20 hours.



^{11}B NMR (96 MHz, CD_2Cl_2) spectra of the reaction of in situ generated compound **1** with methane (10 bar) at 60°C for 20 hours.



(1,3,5) $^{31}P\{^1H\}$ and (2,4,6) ^{31}P NMR (121 MHz, CD_2Cl_2) spectra of the reaction of in situ generated compound **1** with methane (10 bar) at 60°C for 20 hours.

Theoretical Methods and Technical Details of the Computations

All quantum chemical calculations were performed with the TURBOMOLE suite of programs.[1] All minimum structures were fully optimized at the dispersion-corrected Kohn-Sham density functional theory (DFT) level using the TPSS density functional[2] in combination with the polarized triple-zeta (def2-TZVP) sets by Ahlrichs *et al.*[3,4]

We included the atom pairwise D3 correction with BJ-damping to account for intra- and intermolecular London dispersion interactions.[5] The overall level will be denoted as TPSS-D3(BJ)/def2-TZVP

The structures were verified as minima by re-optimization and subsequent harmonic frequency calculation at the HF-3c level.[6] This composite method combines Hartree-Fock in a minimal basis with the above mentioned D3 correction (BJ-damping) as well as two geometrical correction terms that reduce errors of the small basis set, namely the geometrical counterpoise correction (gCP)[7] and a short-range basis set correction.[6] The entire scheme is available in the TURBOMOLE suite of programs (version 7.0.2).

We furthermore exploit the efficiency of this method to find and optimize transition state structures. Transition state structures found with HF-3c (verified as such by a single vibrational mode with imaginary frequency) are then re-optimized at the TPSS-D3(BJ)/def2-TZVP following the modes as they are obtained from the HF-3c Hessian. The transition state structures obtained this way are verified as such also on the TPSS-D3(BJ)/def2-TZVP potential energy surface by a harmonic frequency calculation at this level of theory.

The electronic energies presented in this work were obtained by applying the PW6B95 meta-hybrid density functional[8] along with the D3(BJ) correction[5] and the large polarized quadruple-zeta (def2-QZVP) sets by Ahlrichs *et al.*[4,9] to the geometries obtained by TPSS-D3(BJ)/def2-TZVP.

In all DFT treatments, the resolution-of-the-identity approximation has been employed[10] for the Coulomb integrals to speed up the computations. The numerical quadrature grid *m5* was used for the integration of the exchange-correlation potential. We report pure electronic energies including D3 dispersion (termed ΔE) as well as free energies at 298.15 K and 1 atm (termed ΔG). The ro-vibrational contribution to the free energy are obtained from a modified rigid rotor, harmonic

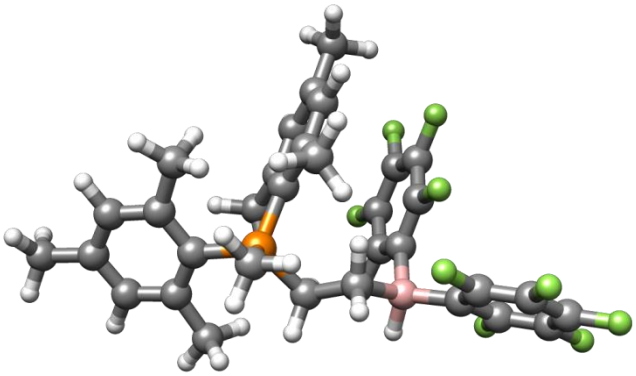
oscillator statistical treatment[11] based on the harmonic frequencies (scaled by 0.86) obtained at the HF-3c level (see above). In the entropy calculations, all frequencies with wavenumbers below 100 cm^{-1} were treated as mixed rigid rotors and harmonic oscillators as described in Ref. [11].

Solvation contributions to the free energies were computed with the COSMO-RS method[12] (COSMOtherm software package[13]) based on BP86/TZVP[14] calculations (parametrization from 2012) at 298.15 K in dichloromethane solution based on the TPSS-D3(BJ)/def2-TZVP gas phase structures.

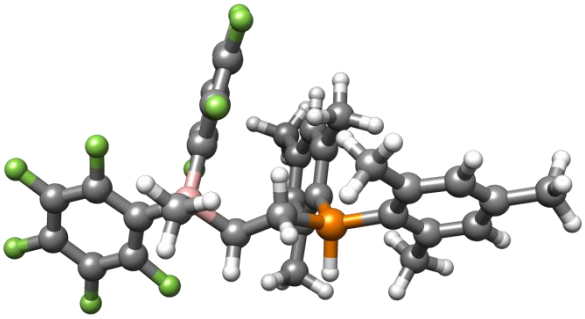
The computed reaction free energies are then obtained by

$$\Delta G = \Delta E + \Delta G_{RRHO} + \Delta\delta G_{COSMO\text{-}RS}\,.$$

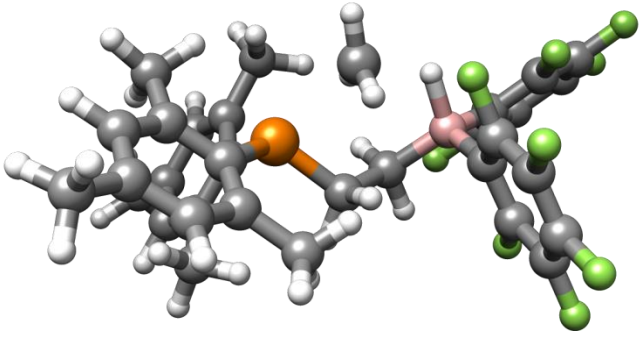
Here, the last two terms refer to the difference in the ro-vibrational and solvation contributions, respectively, to the free energy while the first term on the right hand side refers to the difference in electronic energies as computed at the PW6B95-D3(BJ)/def2-QZVP//TPSS-D3(BJ)/def2-TZVP level.



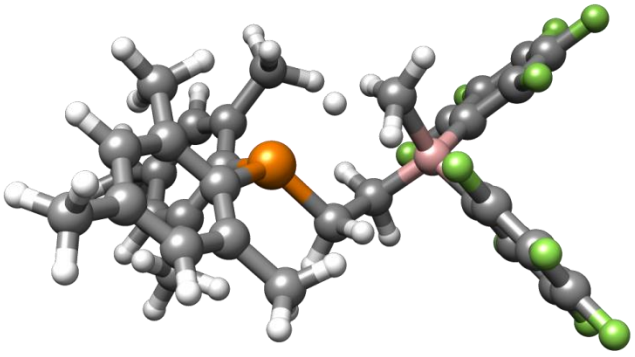
compound **6**



compound **9**



TS **6**/**1**+CH_4



TS **9**/**1**+CH_4

Figure S1: Ball-and-stick representations of the formal CH_4 addition products to FLP **1**: compound **6** and **9** (top left and right, respectively). The transition state structures for the respective CH_4 elimination reactions are depicted in the bottom part. Color code: boron=pink, carbon=grey, fluorine=green, hydrogen=white, and phosphorus=orange.

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Thermodynamic data

(PW6B95-D3(BJ)/def2-QZVP//TPSS-D3(BJ)/def2-TZVP, dichloromethane , 298.15 K, HF-3c frequencies, total energies in Hartree, relative energies in kcal/mol):

compound **1**	+ CH_4	->	compound **6**	
-2603.76585	-40.58481	-2644.34208	5.38	E_gas(tot)
-0.02661	0.00551	-0.04013	-11.94	G_solv
0.43567	0.02788	0.47974	10.16	G_rovib
-2603.35679	-40.55142	-2643.90247	3.60	G_tot_solution

compound **1**	+ CH_4	->	compound **9**	
-2603.76585	-40.58481	-2644.33669	8.76	E_gas(tot)
-0.02661	0.00551	-0.03887	-11.15	G_solv
0.43567	0.02788	0.47842	9.33	G_rovib
-2603.35679	-40.55142	-2643.89714	6.94	G_tot_solution

compound **6**	-> TS **6/1**+CH_4		
-2644.34208	-2644.23033	70.12	E_gas(tot)
-0.04013	-0.03308	4.42	G_solv
0.47974	0.47614	-2.26	G_rovib
-2643.90247	-2643.78727	72.29	G_tot_solution
compound **9**	-> TS **9/1**+CH_4		
-2644.33669	-2644.25410	51.82	E_gas(tot)
-0.03887	-0.03227	4.15	G_solv
0.47842	0.47531	-1.95	G_rovib
-2643.89714	-2643.81105	54.02	G_tot_solution

Cartesian coordinates of the investigated systems

In Ångström (TPSS-D3(BJ)/def2-TZVP):

compound **1**

70

C	-2.3987224	0.2357803	-1.7653250
H	-2.8376697	1.0184458	-2.3913425
B	-0.8003052	0.0041157	-2.0648314
C	-2.4384671	0.6487417	-0.2708391
H	-2.9885346	-0.6655419	-1.9354411
H	-3.1925049	0.1642400	0.3452646
P	-0.6569156	0.3472454	0.1294961
H	-2.5506261	1.7307711	-0.1592511
C	-0.1787128	1.7200856	1.2513894
C	-0.2570218	-1.2272343	0.9959276
C	-0.2473829	-1.5079662	-2.1471682
C	-0.1113625	1.0881707	-3.0271800
C	0.7950027	2.6692284	0.8860112
C	1.0518749	3.7445859	1.7450871
C	0.3887555	3.8997151	2.9587608
C	-0.5555860	2.9311646	3.3158671
C	-0.8586585	1.8495301	2.4903604
C	1.6288870	2.5691262	-0.3660827
H	1.8057235	4.4733583	1.4525898
C	0.6672613	5.0761603	3.8593872
H	-1.0754184	3.0185221	4.2682912
C	-1.9007660	0.8633675	2.9599808
C	1.0645735	-1.3812163	1.4955111
C	1.4825485	-2.6311209	1.9596425
C	0.6566064	-3.7520793	1.9423659
C	-0.6480003	-3.5761147	1.4850701
C	-1.1271000	-2.3490962	1.0194662
C	2.0833826	-0.2689635	1.5542428
H	2.5042744	-2.7275889	2.3205937
C	1.1632022	-5.1076775	2.3602848

H	-1.3275746	-4.4259516	1.4783110
C	-2.5780628	-2.3174872	0.6052843
C	0.6892090	0.7829199	-4.1354076
C	1.2096071	1.7467725	-4.9985441
C	0.9360504	3.0922401	-4.7749454
C	0.1388391	3.4513423	-3.6910823
C	-0.3631875	2.4549228	-2.8640481
F	0.9873423	-0.4982751	-4.4462736
F	1.9670808	1.3885326	-6.0507355
F	1.4334016	4.0329235	-5.5920796
F	-0.1210684	4.7503862	-3.4487787
F	-1.1084744	2.8728536	-1.8077700
C	1.0758610	-1.7844496	-1.7874948
C	1.5998869	-3.0598979	-1.6382502
C	0.7809101	-4.1574904	-1.8899228
C	-0.5271687	-3.9454103	-2.3088586
C	-1.0077208	-2.6431496	-2.4386792
F	1.9145844	-0.7489142	-1.5320986
F	2.8726869	-3.2485724	-1.2436637
F	1.2530881	-5.4057524	-1.7349176
F	-1.3216051	-4.9997559	-2.5754688
F	-2.2865061	-2.5343851	-2.8810034
H	-2.8263773	0.9576103	2.3815264
H	-1.5537677	-0.1697922	2.8623136
H	-2.1461192	1.0475627	4.0091116
H	2.6899718	2.4831371	-0.1040571
H	1.3626700	1.7070381	-0.9792415
H	1.5177698	3.4727172	-0.9741547
H	0.7461938	4.7639108	4.9060163
H	1.5954687	5.5802774	3.5765517
H	-0.1453584	5.8107345	3.7985788
H	3.0757060	-0.6936074	1.7269881
H	2.1245807	0.2988752	0.6245188
H	1.8634285	0.4331607	2.3646149
H	-2.7276242	-1.9056427	-0.3932674
H	-2.9793171	-3.3337694	0.6050915
H	-3.1752749	-1.7255447	1.3078658

H	0.3633100	-5.7152896	2.7942364
H	1.5558941	-5.6506667	1.4912090
H	1.9733285	-5.0218687	3.0903955

CH_4

5

C	0.0000000	0.0000000	0.0000000
H	-0.6308844	0.6308844	0.6308844
H	0.6308844	-0.6308844	0.6308844
H	-0.6308844	-0.6308844	-0.6308844
H	0.6308844	0.6308844	-0.6308844

compound **6**

75

C	-4.8017713	1.8670321	2.3234232
C	-3.4101516	1.9725875	2.2449076
C	-2.8200388	2.5746753	3.3542939
C	-3.5319917	3.0533105	4.4524021
C	-4.9168061	2.9285574	4.4746107
C	-5.5600338	2.3253932	3.3971674
B	-2.6507377	1.4108810	0.9104655
C	-2.6850328	-0.2366191	0.8922075
C	-2.2992462	-0.9963860	1.9986173
C	-2.3148389	-2.3862091	2.0335125
C	-2.6947164	-3.0905190	0.8956825
C	-3.0596119	-2.3863659	-0.2458401
C	-3.0511242	-0.9922746	-0.2208692
F	-1.8630090	-0.3760143	3.1261413
F	-1.9370981	-3.0624969	3.1422651
F	-2.6690303	-4.4398861	0.8889206
F	-3.3890762	-3.0643634	-1.3691313
F	-3.4037306	-0.3787882	-1.3842363
F	-1.4635997	2.7169926	3.4277312
F	-2.8956703	3.6286468	5.4968454

F	-5.6264147	3.3831354	5.5260888
F	-6.9035979	2.1956900	3.4105457
F	-5.4850589	1.2792581	1.3095039
C	-1.0698833	1.8503110	0.7765411
C	-0.6187696	1.5571785	-0.6730209
P	1.1034349	0.9822799	-0.6287480
C	1.0780364	-0.5828833	0.2877356
C	1.4951143	-0.7315155	1.6333096
C	1.4592911	-2.0038527	2.2061627
C	1.0269793	-3.1326204	1.5092514
C	0.5947702	-2.9555083	0.1957311
C	0.6047336	-1.7105343	-0.4340589
C	1.9891451	0.3965202	2.5064640
C	0.9841758	-4.4873291	2.1637532
C	0.1280609	-1.6743875	-1.8685035
C	2.0179241	0.6938952	-2.1840473
C	3.2833579	0.0564409	-2.0944032
C	4.0162113	-0.1578751	-3.2639606
C	3.5472471	0.2228047	-4.5206953
C	2.3054432	0.8543704	-4.5833602
C	1.5286891	1.1022344	-3.4489717
C	3.8997186	-0.4489694	-0.8091340
C	4.3446562	-0.0567796	-5.7678811
C	0.2035909	1.7927966	-3.6679368
H	-3.2486717	1.8238028	-0.0609597
C	1.9966168	2.3783643	0.1231042
H	-0.7071320	2.4476304	-1.2959727
H	-1.2314659	0.7719543	-1.1223481
H	-0.8986632	2.9110894	0.9874704
H	-0.4674341	1.2819707	1.4955375
H	4.9879003	-0.6404550	-3.1812346
H	1.9194188	1.1713504	-5.5495962
H	4.9794030	-0.5580250	-0.9412241
H	3.4895296	-1.4265577	-0.5350014
H	3.7334095	0.2122478	0.0440103
H	5.4193742	0.0122899	-5.5750359
H	4.0868247	0.6419321	-6.5685664

H	4.1404820	-1.0708999	-6.1335535
H	0.0421944	1.9423496	-4.7377839
H	0.1715411	2.7773453	-3.1898196
H	-0.6377528	1.2100514	-3.2829756
H	1.7760234	-2.1098402	3.2408876
H	0.2227649	-3.8113738	-0.3628868
H	2.2219591	0.0108900	3.5011149
H	1.2352322	1.1800497	2.6265815
H	2.9009530	0.8571070	2.1113257
H	1.1823828	-5.2821318	1.4385918
H	-0.0085002	-4.6679137	2.5910434
H	1.7149020	-4.5584749	2.9743232
H	-0.5502518	-2.5120584	-2.0465351
H	0.9677507	-1.7610705	-2.5667411
H	-0.4147452	-0.7614468	-2.1214150
H	3.0546018	2.1646804	0.2701561
H	1.9034864	3.1876811	-0.6092044
H	1.5283265	2.6846471	1.0572247

compound **9**

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P	1.3477221	0.7975560	-0.6283132
H	2.1116856	1.7302119	0.0789925
B	-2.4235415	1.6423371	0.8372182
C	-0.3080587	1.5154112	-0.6829169
H	-0.2763273	2.4271872	-1.2850895
H	-0.9681035	0.8035390	-1.1862764
C	-0.7713856	1.7833012	0.7635950
H	-0.4192783	2.7763474	1.0618655
H	-0.3169379	1.0574549	1.4464807
C	-3.1050701	2.7613713	-0.1389358
H	-2.7254917	2.7395920	-1.1697842
H	-2.8873828	3.7627261	0.2607799
H	-4.1946852	2.6741305	-0.2078406
C	2.2647220	0.5593310	-2.1750025
C	3.6566444	0.3103811	-2.0509951

C	4.4129608	0.1094097	-3.2046323
H	5.4792027	-0.0792040	-3.1000635
C	3.8428793	0.1458195	-4.4788242
C	2.4754995	0.4057319	-4.5757801
H	2.0131516	0.4485960	-5.5592778
C	1.6646042	0.6156908	-3.4568622
C	4.3583972	0.2683633	-0.7163529
H	5.4127926	0.0181243	-0.8523636
H	3.9140512	-0.4747279	-0.0459331
H	4.3132594	1.2409613	-0.2103584
C	4.6747189	-0.1093427	-5.7083674
H	5.6884373	0.2846851	-5.5898491
H	4.2231087	0.3451458	-6.5943431
H	4.7604966	-1.1873000	-5.8943365
C	0.2008866	0.8902477	-3.7055381
H	-0.0097627	0.8109952	-4.7741914
H	-0.0867790	1.8953599	-3.3845015
H	-0.4497914	0.1811173	-3.1871301
C	1.3571973	-0.6715687	0.4131276
C	1.8288043	-0.5951114	1.7478892
C	1.7816920	-1.7507524	2.5283360
H	2.1286940	-1.6933481	3.5572682
C	1.2829559	-2.9616946	2.0442667
C	0.8282778	-3.0072734	0.7248245
H	0.4175375	-3.9347086	0.3333271
C	0.8434267	-1.8855563	-0.1009563
C	2.3522297	0.6717739	2.3821342
H	2.6335544	0.4751088	3.4188550
H	1.5954025	1.4630376	2.3875173
H	3.2400492	1.0551881	1.8654524
C	1.1823758	-4.1697868	2.9355435
H	1.3278697	-5.0947223	2.3698324
H	0.1837950	-4.2131301	3.3870276
H	1.9161640	-4.1308193	3.7453807
C	0.2707031	-1.9990767	-1.4896400
H	-0.0841553	-3.0156495	-1.6712315
H	1.0076846	-1.7502441	-2.2598087

H	-0.5913219	-1.3325424	-1.6092377
C	-2.7128948	0.0505034	0.4245502
C	-2.3459395	-0.9814884	1.2958634
C	-2.5237184	-2.3361199	1.0321821
C	-3.0713804	-2.7282179	-0.1846283
C	-3.4377260	-1.7502130	-1.1013230
C	-3.2536995	-0.4038100	-0.7808483
C	-3.0202828	1.8704043	2.3610854
C	-2.3305311	2.3588220	3.4695953
C	-2.9048603	2.5622619	4.7231260
C	-4.2499789	2.2698579	4.9156632
C	-4.9911759	1.7785115	3.8452685
C	-4.3681252	1.5957028	2.6140276
F	-1.7621193	-0.6922105	2.4896035
F	-2.1540650	-3.2783415	1.9288890
F	-3.2200806	-4.0356643	-0.4776358
F	-3.9490755	-2.1159632	-2.2967840
F	-3.6303513	0.4728492	-1.7497101
F	-1.0008611	2.6642773	3.3894842
F	-2.1696976	3.0356057	5.7536526
F	-4.8265594	2.4599353	6.1182787
F	-6.2978826	1.4875793	4.0158677
F	-5.1545560	1.1060434	1.6188116

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C	-0.6405672	0.5032909	-1.6889118
H	-0.3335311	1.5300246	-1.4453892
B	0.2439373	-0.1460096	-2.9217276
C	1.9432379	-0.0992438	-0.9675444
H	3.0235084	-0.1647644	-0.8538973
H	1.5094916	0.8701835	-1.0758798
H	1.5366456	-0.1827178	-2.5776359

C	-0.7854725	-0.3334114	-0.3780512
H	-1.6599867	0.6199087	-2.0738371
H	-0.6728028	-1.3942778	-0.6172777
P	0.4467935	0.0829618	0.9607012
H	1.4009037	-1.0217546	-0.9349440
H	-1.7873758	-0.2020812	0.0405338
C	-0.1979570	1.6708738	1.6271948
C	0.4779386	-1.1064368	2.3501022
C	-0.1731975	-1.7052252	-3.1599579
C	0.3090768	0.6965685	-4.3027488
C	0.4610305	2.8825409	1.3144607
C	-0.0510364	4.0867925	1.8055789
C	-1.1969511	4.1380425	2.5976304
C	-1.8276367	2.9316046	2.9063497
C	-1.3562307	1.7003025	2.4452548
C	1.7064207	2.9530558	0.4641390
H	0.4681944	5.0108492	1.5593272
C	-1.7515031	5.4521228	3.0847268
H	-2.7206039	2.9423887	3.5286913
C	-2.1090188	0.4650108	2.8754566
C	1.3505995	-0.7316149	3.4070104
C	1.4959748	-1.5699871	4.5142830
C	0.8274395	-2.7880896	4.6145718
C	0.0007491	-3.1578492	3.5519429
C	-0.1877502	-2.3579000	2.4226167
C	2.1463134	0.5507306	3.3890211
H	2.1625041	-1.2578364	5.3160271
C	1.0128611	-3.6915109	5.8066186
H	-0.5272905	-4.1083928	3.5988422
C	-1.1090669	-2.9051727	1.3577466
C	1.0931491	0.2172697	-5.3605031
C	1.2278900	0.8615839	-6.5853139
C	0.5565922	2.0636717	-6.7967333
C	-0.2292222	2.5913715	-5.7774218
C	-0.3327589	1.9099722	-4.5659794
F	1.7882477	-0.9356216	-5.2057268
F	1.9996310	0.3470061	-7.5616029

F	0.6717318	2.7085733	-7.9695182
F	-0.8814110	3.7543629	-5.9723388
F	-1.1207349	2.4964838	-3.6289674
C	0.6243692	-2.8248901	-2.9242403
C	0.1876912	-4.1371941	-3.1001040
C	-1.1098675	-4.3727896	-3.5426506
C	-1.9464417	-3.2902105	-3.8031510
C	-1.4648809	-1.9993117	-3.6069824
F	1.9098647	-2.6832756	-2.5028445
F	1.0061586	-5.1772713	-2.8477911
F	-1.5509154	-5.6300950	-3.7173685
F	-3.2029342	-3.5058366	-4.2362449
F	-2.3245411	-0.9846726	-3.8797088
H	-2.2344366	-0.2520460	2.0606308
H	-1.5837587	-0.0584040	3.6813262
H	-3.1020161	0.7426794	3.2389355
H	2.2253850	3.8998381	0.6350914
H	2.3969219	2.1341839	0.6818962
H	1.4601118	2.9089634	-0.6043494
H	-2.2037376	5.3496255	4.0759297
H	-0.9718727	6.2177275	3.1340536
H	-2.5310387	5.8159639	2.4035446
H	2.9454574	0.5067646	4.1338296
H	2.6016325	0.7212008	2.4058552
H	1.5207363	1.4224425	3.6083931
H	-0.5675709	-3.1509813	0.4375749
H	-1.5758172	-3.8257232	1.7166938
H	-1.9072099	-2.2059700	1.0953941
H	0.0559295	-4.1040649	6.1430625
H	1.6622327	-4.5390620	5.5544386
H	1.4717918	-3.1552413	6.6418661

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75

C	-1.1571119	0.8418091	-1.0996544
H	-0.7592353	1.7013429	-0.5471657

B	-0.4676137	0.6741156	-2.5803670
C	1.2223208	0.1985331	-2.1426615
H	1.9918778	0.0266893	-2.8870348
H	1.2984398	1.1427388	-1.6145464
H	0.6946056	-0.7140945	-1.8718230
C	-1.0453179	-0.4280833	-0.2109951
H	-2.2245115	1.0589233	-1.2229705
H	-1.0514033	-1.3268791	-0.8374060
P	0.5365649	-0.3904488	0.7696008
H	1.4892134	-0.1501008	-0.8438817
H	-1.8953578	-0.5107193	0.4715076
C	0.2214003	0.9475496	1.9834222
C	0.8864160	-1.9144020	1.7216998
C	-1.2680379	-0.4975102	-3.4058597
C	-0.3070863	2.0096613	-3.4976682
C	0.8477304	2.2008714	1.7944570
C	0.6057927	3.2313582	2.7069385
C	-0.2381974	3.0646775	3.8043463
C	-0.8418787	1.8175833	3.9795423
C	-0.6312960	0.7551349	3.0979939
C	1.7684888	2.4917618	0.6336989
H	1.0945333	4.1910501	2.5512708
C	-0.5123675	4.2004723	4.7567117
H	-1.5026173	1.6615837	4.8304445
C	-1.3166328	-0.5546944	3.4010234
C	2.0456494	-1.8339153	2.5384366
C	2.4390407	-2.9417066	3.2913159
C	1.7412418	-4.1480762	3.2542025
C	0.6250523	-4.2208164	2.4202286
C	0.1825782	-3.1416053	1.6500219
C	2.8872144	-0.5840238	2.6307236
H	3.3248088	-2.8540171	3.9178384
C	2.1990388	-5.3426091	4.0515762
H	0.0673102	-5.1536928	2.3637143
C	-1.0327335	-3.3788791	0.7849974
C	0.3157278	1.9162022	-4.7469020
C	0.5178380	2.9941618	-5.6025140

C	0.0830316	4.2584239	-5.2128279
C	-0.5415857	4.4102783	-3.9793693
C	-0.7222023	3.2984661	-3.1576004
F	0.7714909	0.7110751	-5.1779975
F	1.1291979	2.8336212	-6.7915298
F	0.2687434	5.3186486	-6.0169102
F	-0.9676717	5.6286605	-3.5930853
F	-1.3520139	3.5368003	-1.9783714
C	-0.8917514	-1.8249404	-3.6066567
C	-1.6591193	-2.7649715	-4.2909407
C	-2.8895872	-2.3870155	-4.8165098
C	-3.3272199	-1.0774710	-4.6362515
C	-2.5225361	-0.1802778	-3.9402646
F	0.2948074	-2.2963443	-3.1107302
F	-1.2264607	-4.0319723	-4.4396103
F	-3.6499613	-3.2751806	-5.4773464
F	-4.5218024	-0.6997929	-5.1270120
F	-3.0215610	1.0709454	-3.7808981
H	-1.7255750	-1.0255942	2.5035524
H	-0.6204124	-1.2727704	3.8473333
H	-2.1377624	-0.3927336	4.1045620
H	2.3948954	3.3603983	0.8532861
H	2.4202538	1.6434879	0.4053969
H	1.1937979	2.7301399	-0.2709345
H	-0.6307566	3.8388463	5.7828316
H	0.2953649	4.9377196	4.7375599
H	-1.4401969	4.7174565	4.4812477
H	3.8635740	-0.8194338	3.0627230
H	3.0491782	-0.1387760	1.6414650
H	2.4125354	0.1821552	3.2529579
H	-0.7861012	-3.3332562	-0.2811510
H	-1.4368591	-4.3742562	0.9851392
H	-1.8270981	-2.6519943	0.9738566
H	1.3579103	-5.9933697	4.3087372
H	2.9151733	-5.9416931	3.4748378
H	2.6967944	-5.0352253	4.9762477